Structural Aspects of Co-ordinated Nitrate Groups

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1 Introduction

The field of nitrate chemistry has expanded rapidly over the past 10—15 years since the realisation that the nitrate group is capable of behaving as a reasonably strong complexing agent.[1,2] A wide range of nitrato-complexes has now been characterised[3,4,5] and in recent years the structures of a considerable number of these have been established by diffraction techniques. We feel therefore that this is a suitable time to summarise the knowledge presently available from these structural studies.

In this review we are concerned primarily with compounds in which an appreciable and specific metal–nitrate interaction has been identified. The factors that determine the mode of co-ordination adopted by nitrato-groups and the stereochemistry of compounds that contain bidentate nitrato-groups are considered. The dimensions of nitrato-groups are then reviewed and finally two of the more important properties of nitrato-groups, namely their vibrational spectra and chemical reactivity, are discussed in relation to the structural data.

2 Modes of Co-ordination of Nitrato-groups

The nitrate group has been recognised as a versatile ligand for some time and several modes of co-ordination have been proposed, Figure 1. The structural studies carried out so far have identified four of these types of nitrato-group; symmetrically bidentate, unsymmetrically bidentate, unidentate (C_s), and bridging.

Tables 1, 2, 3, and 4 list the compounds containing nitrato-groups which have had their structures established by diffraction techniques. It is immediately apparent that many more examples of symmetrically bidentate nitrato-groups have been confirmed than of any other type. Sufficient structures have probably been determined to indicate that nitrato-groups in fact show a preference for this mode of co-ordination. It is therefore of interest to examine the factors which

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[1] C. C. Addison and B. J. Hathaway, *J. Chem. Soc.*, 1958, 3099.
[2] D. K. Straub, R. S. Drago, and J. T. Donoghue, *Inorg. Chem.*, 1962, **1**, 848.
[3] C. C. Addison and N. Logan, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 71.
[4] B. O. Field and C. J. Hardy, *Quart. Rev.*, 1964, **18**, 361.
[5] C. C. Addison and D. Sutton, *Progr. Inorg. Chem.*, 1967, **8**, 195.

determine the manner in which a nitrate group co-ordinates in a particular complex.

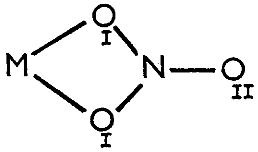
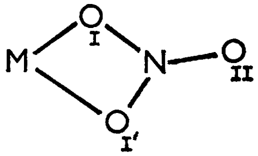
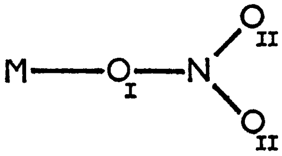
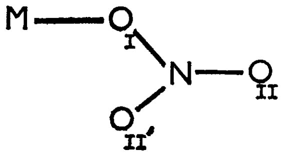
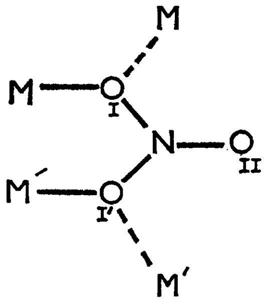
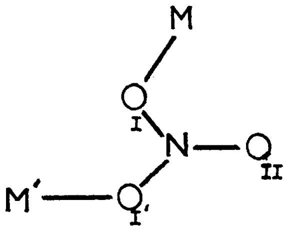
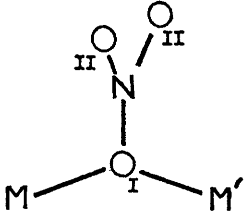
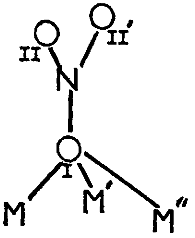
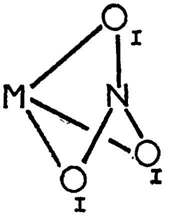
Geometry	Description	Point Group
	Symmetrically Bidentate	C_{2v}
	Unsymmetrically Bidentate	C_s
	Unidentate	C_{2v}
	Unidentate	C_s
	Bridging (*syn-syn or anti-anti*)	C_{2v}

Figure 1 *Possible modes of co-ordination of the nitrate group*

Figure 1 (continued)

	**Bridging** (*syn-anti*)	C_s
	Bridging	C_{2v}
	Bridging	C_s
	Terdentate	C_{2v}

A. Symmetrically Bidentate Nitrato-groups.—For this mode of co-ordination the metal atom is equidistant from the two co-ordinated oxygen atoms of each nitrate group, *e.g.* $Co(NO_3)_3$,[6] Figure 2. The preference of the nitrato-group for

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[6] J. Hilton and S. C. Wallwork, *Chem. Comm.*, 1968, 871.

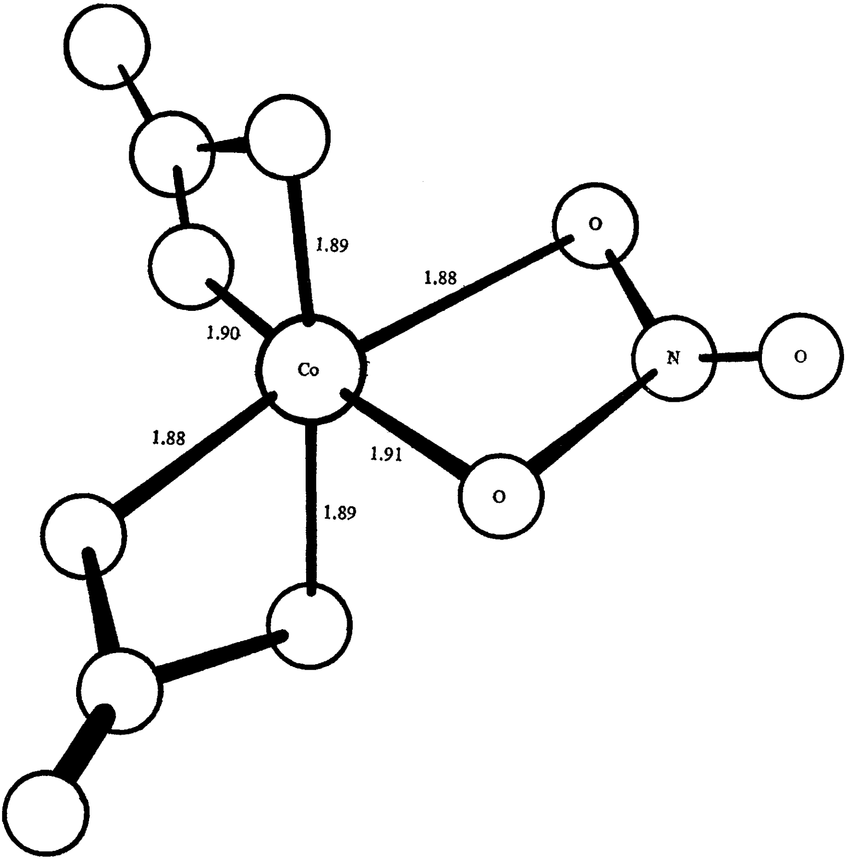

Figure 2 *Structure of* $Co(NO_3)_3$ (*Ref. 6*)

co-ordination as a symmetrically bidentate ligand may be understood in the following way. If the nitrate group is co-ordinated to a metal ion *via* one oxygen atom (O_I), then as shown in Figure 3, there is relatively close approach of another oxygen ($O_{I'}$) to the metal ion. This close approach results from the geometry of the nitrato-group itself, taken together with the value of the MO_IN interbond angle which is normally* between 120 and 109·5°. The electrostatic

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*Some species, *e.g.* $\{[(NH_3)_5Cr]_2O\}^{4+}$,[7] $[(Cl_5Ru)_2O]^{4-}$,[8] and $[TiCl_2(C_5H_5)_2]_2O$[9] do contain linear bonds at the oxygen atom. This behaviour appears to be unusual and can be attributed to extensive (oxygen) $p\pi$–$d\pi$ bonding,[9] a situation not expected in metal-nitrato-complexes.

[7] D. J. Hewkin and W. P. Griffith, *J. Chem. Soc.* (A), 1966, 472.

[8] A. M. Mathieson, D. P. Mellor, and N. C. Stephenson, *Acta Cryst.*, 1952, **5**, 185.

[9] P. Corradini and G. Allegra, *J. Amer. Chem. Soc.*, 1959, **81**, 5510.

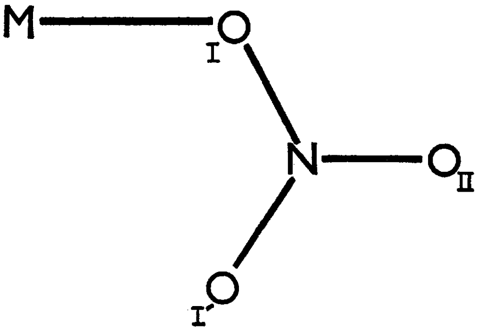

Figure 3

attraction between the metal ion and $O_{I'}$ will tend to shorten the distance M–$O_{I'}$ and, in the extreme, give symmetrically bidentate co-ordination of the nitrato-group. Alternatively, it may be argued that, because of the electronegative nature of oxygen, the donation of electronic charge to the metal from a single oxygen would be less favourable than the donation of rather less charge by each of two oxygens.

This tendency to donate charge from two oxygen atoms is also satisfied by bridging co-ordination. However, the ligand–ligand repulsions will be greater if a given metal co-ordination is achieved using bridging rather than bidentate nitrato-groups because the bridging situation cannot take advantage of the short 'bite' of the nitrato-groups. Thus, the symmetrically bidentate co-ordination of nitrato-groups maximises the metal–nitrate interaction for a given degree of nitrate–nitrate repulsion. The occurrence of this mode of bonding in the wide variety of compounds listed in Table 1 may therefore be readily understood.

These arguments should also apply to complexes of carbonate, acetate, and similar groups. Indeed, several examples of bidentate carbonato-groups have been confirmed.[10] It has been suggested,[11] however, that co-ordination as a bidentate ligand is unusual for acetate groups. Certainly in a large number of instances they co-ordinate as bridging ligands.[12] Nevertheless, there are examples of symmetrically bidentate acetato-groups[13] and in many of the compounds

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[10] *E.g.* K. Nakamoto, J. Fujita, and A. E. Martell, *J. Chem. Phys.*, 1962, **36**, 339; G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.*, 1962, 586; F. Cariati, R. Mason, G. B. Robertson, and R. Ugo, *Chem. Comm.*, 1967, 408; D. B. Shinn and H. A. Eick, *Inorg. Chem.*, 1968, **7**, 1340; K. V. Krishnamurthy, G. M. Harris, and V. S. Sastri, *Chem. Rev.*, 1970, **70**, 171.

[11] C. Oldham, *Progr. Inorg. Chem.*, 1968, **10**, 223.

[12] *E.g.* J. K. Kochi and R. V. Subramanian, *Inorg. Chem.*, 1965, **4**, 1527; R. W. Brandon and D. V. Claridge, *Chem. Comm.*, 1968, 677, and references therein.

[13] J. N. van Niekerk, F. R. L. Schoening, and J. H. Talbot, *Acta Cryst.*, 1953, **6**, 720; W. H. Zachariasen and H. A. Plettinger, *Acta Cryst.*, 1959, **12**, 526; B. Kamenar, *Acta Cryst.*, 1963, **16**, A34; P. O. Whimp, M. F. Bailey, and N. F. Curtis, *J. Chem. Soc.* (*A*), 1970, 1956.

where they do not appear, inhibiting factors such as those discussed below seem to be important.

B. Unsymmetrically Bidentate Nitrato-groups.—This situation occurs when there is a small but real difference (*e.g.* 0·2—0·7 Å) between the distances of the metal atom from the two co-ordinated oxygen atoms of each nitrato-group, for example[14] in $[Co(NO_3)_4]^{2-}$, Figure 4.

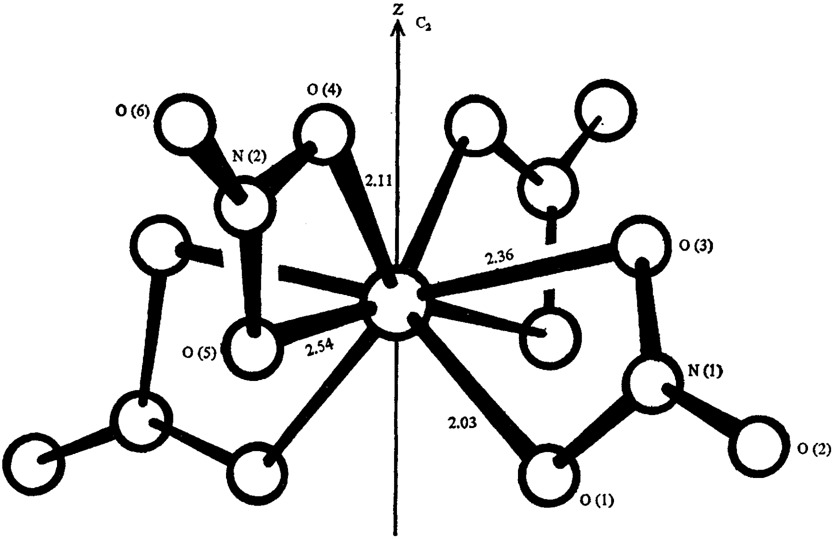

Figure 4 *Structure of* $[Co(NO_3)_4]^{2-}$ (*Ref. 14*)

It is possible to suggest two factors which may lead to unsymmetrically bidentate co-ordination of nitrato-groups:

(i) an electronic distribution at the metal which is unsymmetrical with respect to the two co-ordinated oxygens of each bidentate nitrato-group.

(ii) the presence of a ligand with a strong *trans* effect situated in a position *trans* to only one of the two co-ordinated oxygens of a bidentate nitrato-group.

In some of the compounds in Table 1 the oxygen atoms of the nitrato-groups participate in hydrogen bonding and although the two co-ordinated oxygen atoms may participate to a different extent, hydrogen bonding is not expected to lead to more than a slight asymmetry. This asymmetry

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[14] J. G. Bergman and F. A. Cotton, *Inorg. Chem.*, 1966, **5**, 1208.

will be in the sense that the oxygen participating in the strongest hydrogen bonds will have its other bonds lengthened to the extent of 0·01—0·02 Å.[15]

The above factors will now be considered in more detail.

(i) The structures of the tetranitrato-complexes of Ti^{IV},[16] Mn^{II},[17] Fe^{III},[18] Sn^{IV},[19] and Co^{II} [14] are all eight co-ordinate and correspond closely to the point group D_{2d}. However, whereas $Ti(NO_3)_4$, $[Mn(NO_3)_4]^{2-}$, $[Fe(NO_3)_4]^-$, and $Sn(NO_3)_4$ contain symmetrically bidentate nitrato-groups, $[Co(NO_3)_4]^{2-}$ contains unsymmetrically bidentate groups. This difference does not appear to be a function of the sizes of the ions, their ionic radii for eight co-ordination being, Ti^{4+} 0·70, Mn^{2+} 0·83, Fe^{3+} 0·66, Sn^{4+} 0·74, and Co^{2+} 0·77 Å;[20] rather, it can be related to their electronic configurations.[21] Ti^{IV} d^0, Mn^{II} and Fe^{III} d^5 (high spin) and Sn^{IV} d^{10} have spherically symmetrical charge clouds, but Co^{II} d^7 (high spin) has not. Point charge calculations[22] indicate that if the nitrato-groups were symmetrically bidentate in $[Co(NO_3)_4]^{2-}$ the population of the Co^{II} d-orbitals would probably be $(d_{z^2})^2$, $(d_{x^2-y^2})^2$, $(d_{xz}, d_{yz})^2$, $(d_{xy})^1$. It is expected[17] that the oxygen atoms which are situated near to the xy-plane (Figure 4) will be involved in larger repulsive interactions (with the electron density associated with the $d_{x^2-y^2}$, d_{xy} and the central annulus of the d_{z^2} orbitals) than will the other four co-ordinated oxygens. Hence, the nature of the asymmetry in the co-ordination of the bidentate nitrato-groups may be understood. In this context it is interesting that the ion $[Co(CF_3CO_2)_4]^{2-}$ shows[23] asymmetry in the metal–oxygen bond lengths in the same sense as $[Co(NO_3)_4]^{2-}$, though to a greater extent.

In $Cu(NO_3)_2$(pyrazine)[23a] the co-ordination polyhedron about the Cu^{II} is a distorted octahedron which consists of two nitrogen atoms, and four oxygen atoms belonging to two unsymmetrically bidentate nitrato-groups. Two of the oxygen atoms and the two nitrogen atoms describe a near square parallelogram with the Cu^{II} at its centre approximately 2·0 Å from the four ligand atoms. The two remaining oxygen atoms are located above and below this parallelogram at approximately 2·5 Å from the Cu^{II}. The environment of the Cu^{II} in the compounds $Cu(NO_3)_2(MeCN)_2$[24] and $Cu(NO_3)_2(H_2O)_2.\frac{1}{2}H_2O$[25] is very similar. Both compounds contain a bridging nitrato-group and an unsymmetrically bidentate nitrato-group. The shorter of the two metal–oxygen distances for the latter group is in the xy-plane of the Cu^{II}, whilst the longer (by about 0·5—0·6 Å) is directed close to the z-axis. In all these compounds this inequality in the bond lengths

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[15] M. B. Hossain and D. Van der Helm, *J. Amer. Chem. Soc.*, 1968, **90**, 6607.

[16] C. D. Garner and S. C. Wallwork, *J. Chem. Soc.* (*A*), 1966, 1496.

[17] J. Drummond and J. S. Wood, *J. Chem. Soc.* (*A*), 1970, 226.

[18] A. Morris, Ph.D. Thesis, Nottingham University, 1970; T. J. King, N. Logan, A. Morris, and S. C. Wallwork, *Chem. Comm.*, 1971, in the press.

[19] C. D. Garner, D. Sutton, and S. C. Wallwork, *J. Chem. Soc.* (*A*), 1967, 1949.

[20] L. Pauling, 'Nature of the Chemical Bond', 1960, 3rd Ed., Cornell University Press.

[21] N. Logan, paper presented at the Northern Inorganic Group Meeting, Manchester (England), 1969.

[22] C. D. Garner and F. E. Mabbs, unpublished results.

[23] J. G. Bergman and F. A. Cotton, *Inorg. Chem.*, 1966, **5**, 1420.

[23a] A. Santoro, A. D. Mighell, and C. W. Reimann, *Acta Cryst.*, 1970, **26B**, 979.

[24] B. Duffin, *Acta Cryst.*, 1968, **24B**, 396.

[25] J. Garaj, *Acta Chem. Scand.*, 1968, **22**, 1710; B. Morosin, *Acta Cryst.*, 1970, **B26**, 1203.

is of course consistent with the $3d^9$ electronic configuration of Cu^{II}, the single unpaired electron being in the $3d_{x^2-y^2}$ orbital.

Unsymmetrical bidentate co-ordination of nitrato-groups to Cu^{II} has also been observed in $[Cu(NO_3)_2\,py_2]_2\,py$[26] and $Cu(NO_3)_2(\alpha\text{-picoline})_2$.[27] However, no information has yet been published regarding the detailed co-ordination geometry around the metal in these compounds.

Inspection of Table 1 shows that the majority of compounds which contain symmetrically bidentate nitrato-groups have metal ions with electronic distributions such that both the co-ordinated oxygens of each nitrato-group experience the same repulsion from the electrons of the metal ion. Exceptions are $(Me_3PO)_2Co(NO_3)_2$[28] and $Mg_3[Ce(NO_3)_6]_2.24H_2O$.[29] The former exhibits a significant difference in metal–oxygen bond lengths of 0·09 Å (e.s.d. ± 0·02 Å) for one nitrato-group, the other group having a smaller difference of 0·02 Å in these lengths. For the latter compound, which contains Ce^{III}, $4f^1$, only slight asymmetry in the co-ordination of the nitrato-groups would be expected, and in this context the average difference in the length of the Ce–O bonds of 0·04 Å (e.s.d. 0·008 Å) may be significant.

(ii) The compound $Me_2Sn(NO_3)_2$ might be expected to involve unsymmetrically bidentate nitrato-groups if, for example, the co-ordination of Sn were basically octahedral, with the strongly *trans* directing methyl groups situated *cis* to one another. At the present state of refinement of the crystal structure of this compound[30] it appears that both nitrato-groups are unsymmetrically bidentate, but not, however, in the sense anticipated.

C. Unidentate Nitrato-groups.—In this mode of co-ordination one metal–oxygen distance is so much longer than the other (*e.g.* 0·8—1·1 Å) that there can only be significant bonding between the metal atom and one of the oxygen atoms of each nitrato-group, for example[31] in $[Au(NO_3)_4]^-$, Figure 5.

Unidentate nitrato-groups occur when one or both of the following conditions apply:

(i) the number of metal–nitrate bonds which can be formed is limited to one per nitrato-group;

(ii) the steric interactions with other ligands in the primary co-ordination sphere of the metal prevent bidentate co-ordination of the nitrato-group.

(i) This situation is obtained in the transition metal complexes $Re(CO)_5NO_3$,[30] *cis*-$Pd(NO_3)_2(Me_2SO)_2$,[32] and $K[Au(NO_3)_4]$.[31] The first of these compounds is expected to obey the 'inert gas formalism' which requires the nitrato-group to donate one pair of electrons to Re^I. Similar considerations apply to $Mn(CO)_5NO_3$, which is thus expected to contain a unidentate nitrato-group. In the above com-

[26] A. F. Cameron, K. P. Forrest, R. H. Nuttall, and D. W. Taylor, *Chem. Comm.*, 1970, 210.
[27] A. F. Cameron, R. H. Nuttall, and D. W. Taylor, *Chem. Comm.*, 1970, 865.
[28] F. A. Cotton and R. H. Soderberg, *J. Amer. Chem. Soc.*, 1963, **85**, 2402.
[29] A. Zalkin, J. D. Forrester, and D. H. Templeton, *J. Chem. Phys.*, 1963, **39**, 2881.
[30] J. Hilton and S. C. Wallwork, unpublished results.
[31] C. D. Garner and S. C. Wallwork, *Chem. Comm.*, 1969, 108; *J. Chem. Soc.* (*A*), 1970, 3092.
[32] D. A. Langs, C. R. Hare, and R. G. Little, *Chem. Comm.*, 1967, 1080.

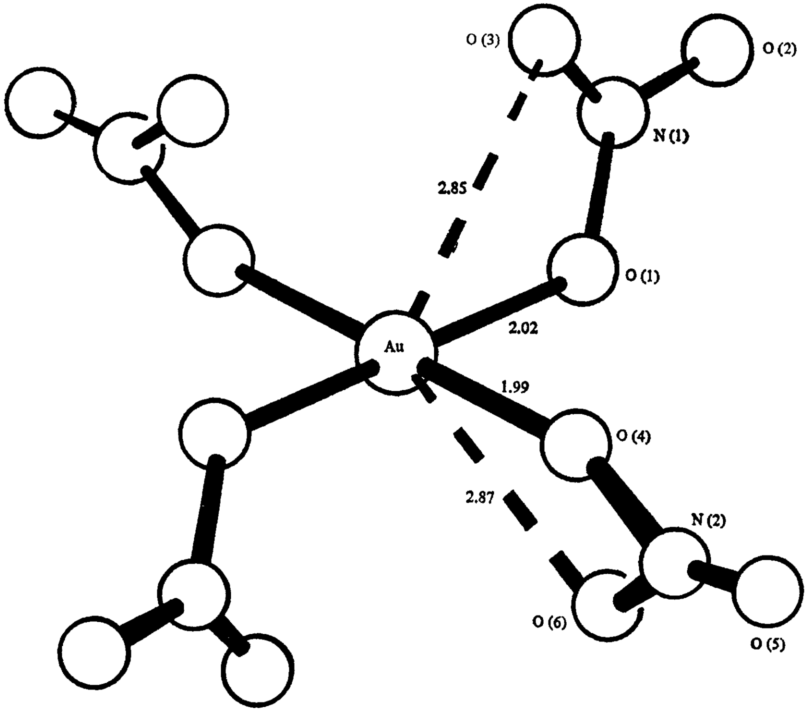

Figure 5 *Structure of* $[Au(NO_3)_4]^-$ (*Ref. 31*)

pounds of Pd^{II}, $4d^8$, and Au^{III}, $5d^8$, the metal ions achieve the expected square-planar co-ordination; each nitrato-group occupies one site and is co-ordinated as a unidentate ligand. Similarly, unidentate nitrato-groups are found in nitric acid,[33] fluorine nitrate,[34] and alkyl nitrates,[34,35] where normal valence considerations require that only one bond be formed to each nitrato-group. It is also interesting that $LiNO_3$ and $NaNO_3$[36] in the vapour phase contain unidentate nitrato-groups. This suggests a specific interaction of the metal with one oxygen of the nitrato-group rather than a general interaction of the two ions.

(ii) In $Re(CO)_5NO_3$,[30] as well as the above mentioned restriction in the number of Re–O bonds, there also appears to be a steric interaction of the nitrato-group with the CO groups causing the oxygen atom ($O_{I'}$, Figure 3) to be even further from the Re^I than would be expected for normal unidentate

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[33] L. R. Maxwell and V. M. Mosley, *J. Chem. Phys.*, 1940, **8**, 738; A. P. Cox and J. M. Riveros, *J. Chem. Phys.*, 1965, **42**, 3106.

[34] L. Pauling and L. O. Brockway, *J. Amer. Chem. Soc.*, 1937, **59**, 13.

[35] A. D. Booth and F. J. Llewellyn, *J. Chem. Soc.*, 1947, 837; J. Trotter, *Acta Cryst.*, 1963, **16**, 698; T. C. W. Mak and J. Trotter, *Acta Cryst.*, 1964, **17**, 367.

[36] A. N. Khodchenkov, V. Spiridonov, and P. A. Akishin, *Zhur. Strukt. Khim.*, 1965, **6**, 765.

nitrato-group geometry. Steric effects also appear to operate in conjunction with bonding restrictions to give unidentate co-ordination of the nitrato-groups in $Ni(NO_3)_2(H_2O)_4$,[37] $Cu(NO_3)_2$(pyridine *N*-oxide)$_2$,[38] $Cu(NO_3)_2.HgO.3H_2O$,[39] $Cu(NO_3)_2$(1,4-diazacycloheptane).$\frac{1}{2}H_2O$,[40] and $Zn(NO_3)_2(H_2O)_4$.[41] Similar considerations lead to the expectation of a unidentate nitrato-group in the complex $[Co(NH_3)_5NO_3]^{2+}$ and indeed the analogous complex $[Co(NH_3)_5CO_3]^+$ does contain a unidentate carbonato-group.[42]

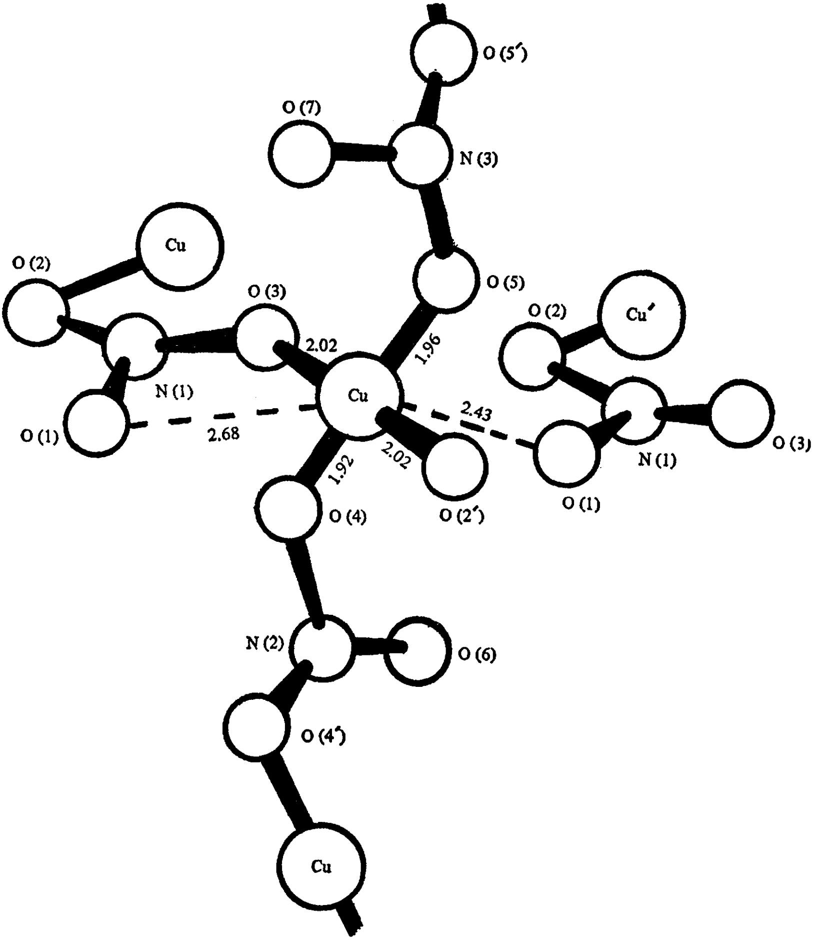

Figure 6 *Structure of* α-$Cu(NO_3)_2$ *(Ref. 43)*

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[37] P. Gallezot, D. Weigel, and M. Prettre, *Acta Cryst.*, 1967, **22**, 699.
[38] S. Scavnicar and B. Matkovic, *Acta Cryst.*, 1969, **25B**, 2046.
[39] B. Kamenar, *Acta Cryst.*, 1969, **25B**, 800.
[40] M. S. Hussain and H. Hope, *Acta Cryst.*, 1969, **25B**, 1866.
[41] B. Ribar, M. Sljukic, B. Matkovic, F. Gabela, and E. Girt, *Acta Cryst.*, 1967, **23**, 1113.
[42] H. C. Freeman and G. Robinson, *J. Chem. Soc.*, 1965, 3194.

D. Bridging Nitrato-groups.—In this situation the nitrate group co-ordinates to more than one metal atom, for example α-$Cu(NO_3)_2$,[43] Figure 6.

The majority of bridging nitrato-groups involve co-ordination by two of the oxygen atoms, each being bonded to a different metal atom; in several of these groups the terminal oxygen atom is also weakly co-ordinated. So far, bridging nitrato-groups have been confirmed only in Ni^{II}, Cu^{II}, and Zn^{II} compounds

Table 1 *Compounds containing symmetrically bidentate nitrato-groups*

Compound	*Average* $(M–O_I) - (M–O_{I'})$ Å
$Ti(NO_3)_4$[a]	0·02
$(Ph_4As)_2[Mn(NO_3)_4]$[b]	0·07
$(Ph_4As)[Fe(NO_3)_4]$[c]	0·01
$Co(NO_3)_3$[d]	0·01
$(Me_3PO)_2Co(NO_3)_2$[e]	0·06
$Cu(NO_3)_2$[f]	0·00
$Cu(NO_3)(Ph_3P)_2$[g]	0·00
$Sn(NO_3)_4$[h]	0·03
$La(NO_3)_3bipy_2$[i]	0·01
$Mg_3[Ce(NO_3)_6]_2.24H_2O$[j]	0·04
$(PPh_3Et)_2[Ce(NO_3)_5]$[k]	0·00
$(NH_4)_2[Ce(NO_3)_6]$[l]	0·02
$Th(NO_3)_4(H_2O)_3.2H_2O$[m,n]	0·06[n]
$Mg[Th(NO_3)_6].8H_2O$[o]	0·00
$[Th(NO_3)_3(H_2O)_3(OH)]_2.2H_2O$[p]	0·10
$Rb[UO_2(NO_3)_3]$[q]	0·00
$Cs[UO_2(NO_3)_3]$[r,s]	0·00
$UO_2(NO_3)_2(H_2O)_2.4H_2O$[t,u,v]	0·00[v]
$UO_2(NO_3)_2(Et_3PO)_2$[w]	0·14
$UO_2(NO_3)_2(Et_3AsO)_2$[x]	0·04
$UO_2(NO_3)_2(H_2O)_2$[y]	0·2
$Pr(NO_3)_3(H_2O)_4.2H_2O$[z]	0·1
$Gd(NO_3)_3$[1,2-di(pyridine-2-aldimino)ethane][aa]	0·1
$Tb(NO_3)_3bipy_2$[bb]	0·03

[a] Ref. 16; [b] Ref. 17; [c] Ref. 18; [d] Ref. 6; [e] Ref. 28; [f] Ref. 52; [g] Ref. 63; [h] Ref. 19; [i] A. R. Al-Karaghouli and J. S. Wood, *J. Amer. Chem. Soc.*, 1968, **90**, 6548; [j] Ref. 29; [k] Ref. 45; [l] Ref. 46; [m] T. Ueki, A. Zalkin, and D. H. Templeton, *Acta Cryst.*, 1966, **20**, 836; [n] Ref. 50; [o] Ref. 47; [p] G. Johansson, *Acta Chem. Scand.*, 1968, **22**, 389; [q] Ref. 53; [r] Ref. 54; [s] Ref. 54[a]; [t] J. E. Fleming and H. Lynton, *Chem. and Ind.*, 1960, 1416; [u] D. Hall, A. D. Rae, and T. N. Waters, *Acta Cryst.*, 1965, **19**, 389; [v] J. C. Taylor and M. H. Mueller, *Acta Cryst.*, 1965, **19**, 536; [w] J. E. Fleming and J. Lynton, *Chem. and Ind.*, 1960, 1415; [x] C. Panattoni, R. Graziani, U. Croatto, B. Zarli, and G. Bombieri, *Inorg. Chim. Acta*, 1968, **2**, 43; [y] V. M. Vdovenko, E. V. Stroganov, A. P. Sokolov, and G. Lungu, *Radiokhimiya*, 1962, **4**, 59; [z] G. F. Volodina, I. M. Rumanova, and N. V. Belov, *Soviet Phys. Cryst.*, 1961, **6**, 741; [aa] Mazhar-ul-Haque, F. A. Hart, and C. N. Caughlan, *Chem. Comm.*, 1970, 1240; [bb] D. S. Moss and S. P. Sinha, *Z. phys. Chem. (Frankfurt)*, 1969, **63**, 190.

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[43] S. C. Wallwork and W. E. Addison, *J. Chem. Soc.*, 1965, 2925.

where they adopt either the *anti-anti* or *syn-anti* conformation (Figure 1). It is likely that they will be identified in compounds of other elements, *e.g.* basic beryllium nitrate $[Be_4O(NO_3)_6]$ appears to have an analogous structure to basic beryllium acetate and therefore to contain bridging nitrato-groups.[43a]

More unusual types of bridging nitrato-groups occur in $[Cu(NO_3)_2\,py_2]_2\,py$[26] and $Cu_4(NO_3)_2(OH)_6$.[44] The former involves bridging of two copper atoms by a single oxygen atom (Table 4). In the latter, each nitrato-group links three copper atoms *via* Cu–O–Cu bridges, the bridging being remarkable since only one oxygen atom in each nitrato-group is involved (see Figure 7). In view of this, further refinement of this structure would be desirable (at present $R = 0{\cdot}30$).

Table 2 *Compounds containing unsymmetrically bidentate nitrato-groups*

Compound	*Average* $(M–O_I) - (M–O_{I'})$ Å (*where published*)
$[Ph_4As]_2[Co(NO_3)_4]$[a]	0·4
$Cu(NO_3)_2(MeCN)_2$[b]	0·6
$Cu(NO_3)_2(H_2O)_2.\frac{1}{2}H_2O$[c]	0·7
$[Cu(NO_3)_2py_2]_2py$[d]	
$Cu(NO_3)_2(\alpha\text{-picoline})_2$[e]	
$Cu(NO_3)_2(\text{pyrazine})$[f]	0·5
$Me_2Sn(NO_3)_2$[g]	0·4

[a] Ref. 14; [b] Ref. 24; [c] Ref. 25; [d] Ref. 26; [e] Ref. 27; [f] Ref. 23a; [g] Ref. 30.

Table 3 *Compounds containing unidentate nitrato-groups*

Compound	*Average* $(M–O_I) - (M–O_{II'})$ Å (*where published*)
$LiNO_3$[a]	
$NaNO_3$[a]	
$Ni(NO_3)_2(H_2O)_4$[b]	0·9†
$Cu(NO_3)_2$(pyridine *N*-oxide)$_2$[c]	0·8
$Cu(NO_3)_2.HgO.3H_2O$[d]	1·1†
$Cu(NO_3)_2(\text{1,4-diazacycloheptane})_2.\frac{1}{2}H_2O$[e]	0·8†
$Zn(NO_3)_2(H_2O)_4$[f]	
$Re(CO)_5(NO_3)$[g]	0·9
cis-$Pd(NO_3)_2(Me_2SO)_2$[h]	
$K[Au(NO_3)_4]$[i]	0·9

†Calculated from atomic positions and unit cell dimensions.

[a] Ref. 36; [b] Ref. 37; [c] Ref. 38; [d] Ref. 39; [e] Ref. 40; [f] Ref. 41; [g] Ref. 30; [h] Ref. 32; [i] Ref. 31.

3 Stereochemistry of Complexes involving Bidentate Nitrato-groups

A. Stereochemistry and Co-ordination Number.—In many of the complexes

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[43a] C. C. Addison and A. Walker, *Proc. Chem. Soc.*, 1961, 242.

[44] W. Nowacki and R. Schiedegger, *Helv. Chim. Acta*, 1952, **35**, 375.

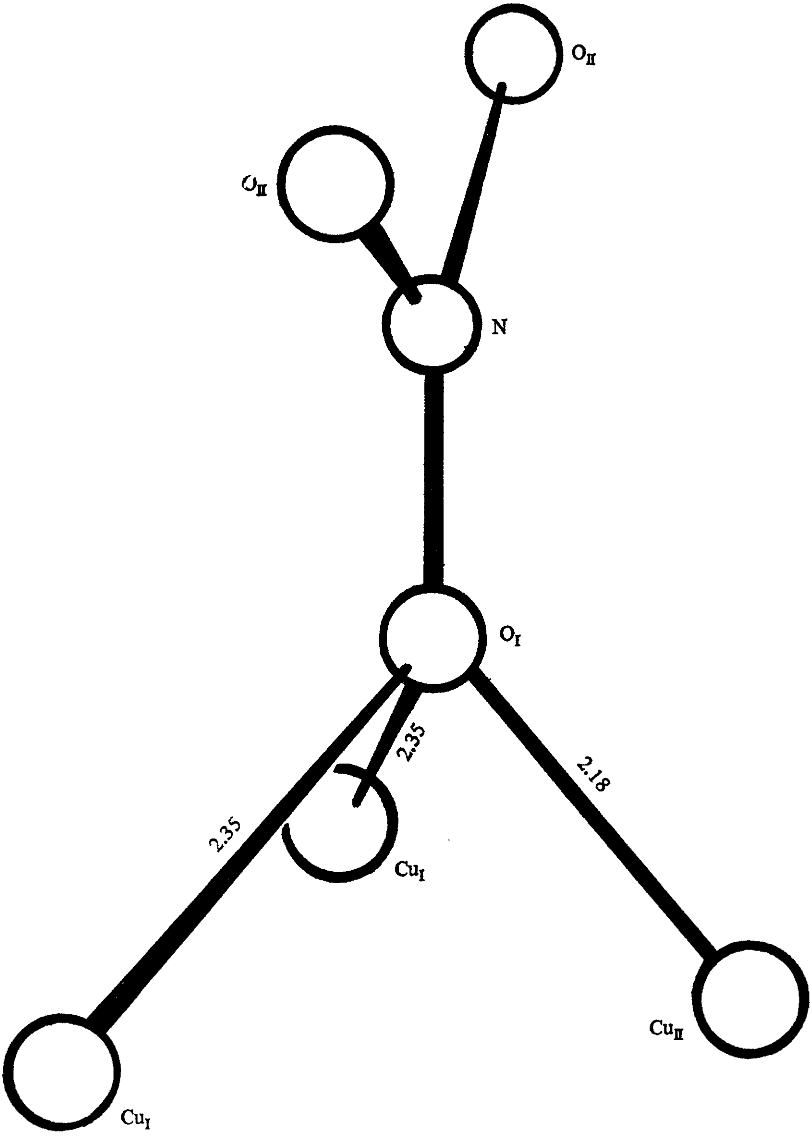

Figure 7 *Environment of the nitrato-groups in* $Cu_4(NO_3)_2(OH)_6$ (*Ref. 44*)

containing bidentate nitrato-groups the metal atom attains an unusually high co-ordination number, *e.g.* Ti^{IV},[16] Mn^{II},[17] Fe^{III},[18] Co^{II},[14] and Sn^{IV} [19] are all eight co-ordinate in their tetranitrato-complexes whilst Ce^{III},[45] Ce^{IV},[46] and Th^{IV} [47] are

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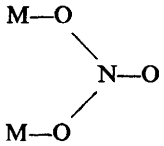
[45] A. R. Al-Karaghouli and J. S. Wood, *Chem. Comm.*, 1970, 135.
[46] T. A. Beineke and J. Delgaudio, *Inorg. Chem.*, 1968, **7**, 715.
[47] S. Scavnicar and B. Prodic, *Acta Cryst.*, 1965, **18**, 698.

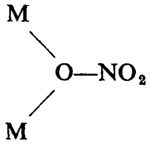
Table 4 *Compounds containing bridging nitrato-groups*

(*a*)



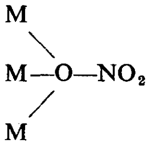
$Ni(NO_3)_2(H_2O)_2$[a]
α-$Cu(NO_3)_2$[b]
$Cu(NO_3)_2(MeNO_2)$[c]
$Cu(NO_3)_2(MeCN)_2$[d]
$Cu(NO_3)_2(H_2O)_2.\frac{1}{2}H_2O$[e]
$Zn(NO_3)_2(H_2O)_2$[f]

(*b*)



$[Cu(NO_3)_2py_2]_2py$[g]

(*c*)



$Cu_4(NO_3)_2(OH)_6$[h]

[a] L. Berger and J. A. Friedberg, *Phys. Rev.*, 1964, **136A**, 158; [b] Ref. 43; [c] B. Duffin and S. C. Wallwork, *Acta Cryst.*, 1966, **20**, 210; [d] Ref. 24; [e] Ref. 25; [f] B. Ribar, W. Nowacki, M. Sljukic, S. Scavnicar, and F. Gabela, *Z. Kristallogr.*, 1969, **129**, 305; [g] Ref. 26; [h] Ref. 44.

all twelve co-ordinate in their hexanitrato-complexes. The occurrence of unusually high co-ordination numbers in these systems can be readily understood since the nitrate group has a short 'bite' of approximately 2·1 Å. Thus, the co-ordinated oxygens have a smaller separation than the sum of their van der Waals radii, which would be approximately their closest approach if they co-ordinated independently.

The stereochemistry of many of these complexes may be correlated with those of simple ligands, for example Cl^-, by considering the repulsions between the nitrato-groups (and other ligands) co-ordinated to the metal ion. Thus, all the tetranitrato-complexes above have the four nitrato-groups located at the vertices of a somewhat distorted tetrahedron, and the arrangement of the nitrato-groups in the hexanitrato-complexes corresponds closely to that of an octahedron. Furthermore, these stereochemistries may be rationalised by the well-known radius-ratio rules.[48] These predict that tetrahedal co-ordination will be obtained

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[48] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', 1966, 2nd Ed., Interscience, p. 47.

if $4{\cdot}44 \geqslant \frac{r_{\text{anion}}}{r_{\text{cation}}} \geqslant 2{\cdot}44$ and octahedral co-ordination if $2{\cdot}44 \geqslant \frac{r_{\text{anion}}}{r_{\text{cation}}} \geqslant 1{\cdot}37$.

Taking a value (2·2 Å) for the radius of the nitrate ion,[49] and the values for the radii of the cations as listed by Pauling,[20] the radius-ratios for the tetranitrato-complexes of Ti^{4+}, Mn^{2+}, Fe^{3+}, Co^{2+}, and Sn^{4+} are 3·14, 2·65, 3·34, 2·86, and 2·98 respectively, whereas those for the hexanitrato-complexes of Ce^{3+}, Ce^{4+}, and Th^{4+} are 1·93, 2·12, and 2·12 respectively.

The repulsions between the nitrato-groups in $[Ce(NO_3)_5]^{2-}$ lead to a trigonal bipyramidal arrangement.[45] Also, the four nitrato-groups and the three co-ordinated water molecules in $Th(NO_3)_4(H_2O)_3.2H_2O$[50] have a distribution about the metal which corresponds closely with that observed for the fluorine atoms in the anion $[NbF_7]^{2-}$.

A natural extension of these structural correlations has been the suggestion[14,16,50,51] that a bidentate nitrate group should be considered as occupying only one co-ordination site of a metal. This idea is also consistent with the magnetic and spectroscopic properties of $[Co(NO_3)_4]^{2-}$[14] and $(Me_3PO)_2Co(NO_3)_2$[51] which closely resemble those for tetrahedral cobalt(II) complexes. However, as a general rule, it would appear that it is better to regard bidentate nitrato-groups as occupying two co-ordination sites of a metal atom rather than one. A number of reasons may be given for this:

(i) Certain complexes, notably $Co(NO_3)_3$,[6] $Cu(NO_3)_2$ (gas phase),[52] and $[UO_2(NO_3)_3]^-$,[53,54,54a] have metal atoms with their normal co-ordination numbers and stereochemistries if each bidentate nitrato-group is considered to form a bond from each of the co-ordinated oxygen atoms to the metal atom. These complexes would, moreover, involve metal atoms with unusually low co-ordination numbers if each bidentate nitrato-group was considered to occupy only one co-ordination site.

(ii) In compounds where the nitrate group is restricted to forming only one bond to the metal (or other) atom, for example $K[Au(NO_3)_4]$,[31] *cis*-$Pd(NO_3)_2(Me_2SO)_2$,[32] $MeNO_3$,[33] HNO_3,[33] it bonds in a unidentate manner.

(iii) Point charge calculations have shown[55] that the crystal-field energy diagram for complexes involving ligands of short 'bite' cannot, in general, be approximated by the replacement of the donor atom of each bidentate

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[49] K. B. Yatsimirskii, *Izvest. Akad. Nauk S.S.S.R. Otdel. khim. Nauk*, 1947, 453; O. J. Kleppa and L. S. Hersh, *Discuss. Faraday Soc.*, 1961, **32**, 157; G. J. Janz and D. W. James, *J. Chem. Phys.*, 1961, **35**, 739; *Electrochim. Acta*, 1962, **7**, 427.

[50] J. C. Taylor, M. H. Mueller, and R. L. Hitterman, *Acta Cryst.*, 1966, **20**, 842; D. Britton and J. D. Dunitz, *Acta Cryst.*, 1965, **19**, 815.

[51] F. A. Cotton, D. M. L. Goodgame, and R. H. Soderberg, *Inorg. Chem.*, 1963, **2**, 1162.

[52] R. E. LaVilla and S. H. Bauer, *J. Amer. Chem. Soc.*, 1963, **85**, 3597.

[53] G. A. Barclay, T. M. Sabine, and J. C. Taylor, *Acta Cryst.*, 1965, **19**, 205.

[54] S. S. Malcic and L. M. Manojlovic, *Bull. Inst. Nuclear Sci.*, '*Boris Kidrich*' (*Belgrade*), 1961, **11**, 135.

[54a] M. S. Zivadinovic, *Bull. Boris Kidrich Inst. Nuclear Sci. Phys.*, 1967, **18**, 1.

[55] C. D. Garner and F. E. Mabbs, *J. Chem. Soc.* (*A*), 1970, 1711.

ligand by a single atom located at their 'centre of gravity'. $[Co(NO_3)_4]^{2-}$ would appear to be a fortuitous case where the *d*-orbital energies in the dodecahedral ligand field of the eight oxygen atoms happen to resemble those for a tetrahedral one.[56]

B. Detailed Geometry.—The effect of the short 'bite' of the bidentate nitrato-group can be seen in the structures of several compounds. One would normally expect a regular octahedral arrangement of ligands around Co^{III}, but in

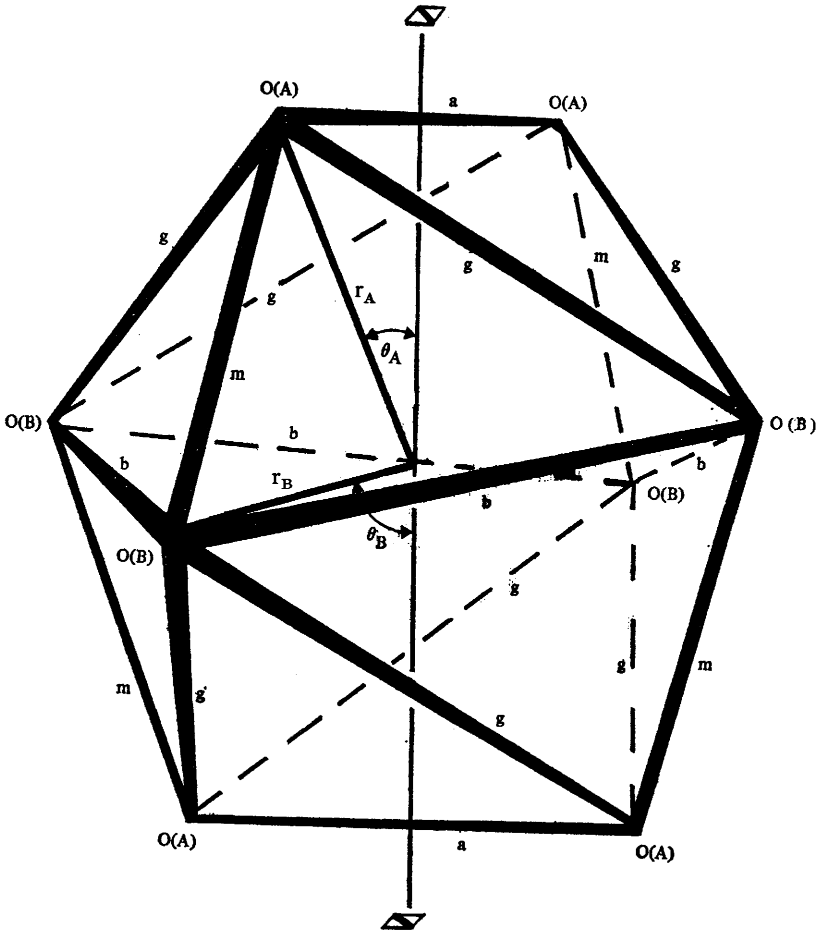

Figure 8 (a) *Trigonal dodecahedron*

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[56] J. Drummond and J. S. Wood, Abstract A34, Chem. Soc. Meeting, Keele, 1968.

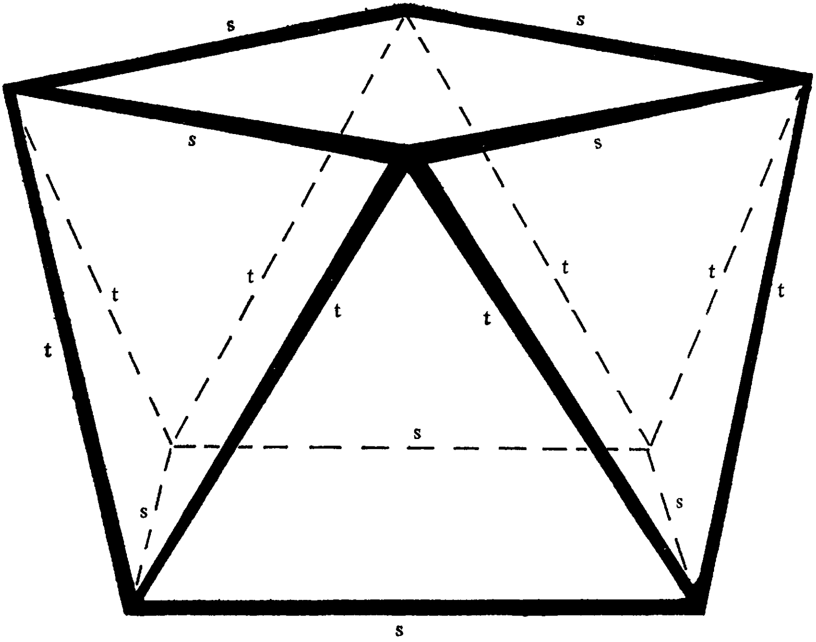

Figure 8 (b) *Square antiprism*

$Co(NO_3)_3$ the arrangement of oxygens is distorted[6] in that the angle subtended at the cobalt by each bidentate nitrato-group is 68° instead of the regular octahedral 90°. Also, in complexes of the uranyl ion the nitrato-groups are able to give a hexagonal arrangement, in the plane perpendicular to this ion, which is only very slightly puckered (± 0·1 Å),[53] whereas other complexes of this ion, *e.g.* UO_2F_2, often involve considerable puckering (± 0·6 Å).[57]

Perhaps the most dramatic effect of this short 'bite' may be seen in the adoption of dodecahedral geometry by the tetranitrato-complexes of Ti^{IV},[16] Mn^{II},[17] Fe^{III},[18] Co^{II},[14] and Sn^{IV}.[19] The two common geometries for eight co-ordinate complexes are the dodecahedron (D_{2d}) and the square antiprism (D_{4d})[58] (Figure 8). Calculations of the energies involved in metal–ligand bonding[59] and ligand–ligand repulsions,[58,60] for eight separate ligands co-ordinated to a central metal, show that these are very similar for the two geometries. However, for compounds such as these tetranitrato-complexes the dodecahedral arrangement reduces the ligand–ligand repulsions much more effectively than does the square antiprismatic one.[19] This is because the square antiprism has

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[57] W. H. Zachariasen, *Acta Cryst.*, 1948, **1**, 277.

[58] J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 1963, **2**, 235.

[59] G. Racah, *J. Chem. Phys.*, 1943, **11**, 214; G. H. Duffey, *ibid.*, 1950, **18**, 746, 1444.

[60] D. L. Kepert, *J. Chem. Soc.*, 1965, 4736; R. V. Parish and P. G. Perkins, *J. Chem. Soc.* (*A*), 1967, 345.

two sets of eight equal edges (the *s* and *t* edges in Figure 8b). Therefore, if the pairs of oxygen atoms linked together in the bidentate nitrato-groups take up four edges out of either set of eight, the distances corresponding to the other four edges are bound to be too close for the non-bonded contacts if the eight distances remain equal. Because of this, a regular square antiprismatic geometry for ligands of short bite is untenable, and the adoption of the dodecahedral arrangement, where no such unfavourable repulsions exist, can be understood.

The dodecahedral shape parameters illustrated in Figure 8a are listed for the $M(NO_3)_4$ species in Table 5. In all the compounds the four *m* edges are necessarily shorter than predicted for the most favourable polyhedron and the other edges correspondingly longer, since the nitrato-groups chelate along the *m* edges. Nevertheless, it is apparent that $Ti(NO_3)_4$, $[Fe(NO_3)_4]^-$, and $Sn(NO_3)_4$ have a closer correspondence to the 'best polyhedron' than have $[Mn(NO_3)_4]^{2-}$ and $[Co(NO_3)_4]^{2-}$, suggesting perhaps that the model is more applicable to complexes involving cations of high charge density. The structure of $[Co(NO_3)_4]^{2-}$ is complicated by the unsymmetrical charge cloud of the Co^{II}, the effects of which, on the metal–oxygen bond lengths, have already been discussed (Section 2B).

Table 5 *Comparison of dodecahedral shape parameters for* $M(NO_3)_4$ *species (average values)*

Parameter[a]	*'Best' polyhedron*[a]	$Ti(NO_3)_4$	$[Mn(NO_3)_4]^{2-}$	$[Fe(NO_3)_4]^-$	$[Co(NO_3)_4]^{2-}$	$Sn(NO_3)_4$
r_A	2·06	2·08	2·27	2·14	2·07	2·18
r_B	2·00	2·06	2·34	2·13	2·45	2·15
r_A/r_B	1·03	1·01	0·97	1·02	0·84	1·01
θ_A	35·2	37·2	43·0	38·7	46·5	38·9
θ_B	75·5	80·7	83·7	81·2	80·5	81·7
a	2·34	2·51	3·09	2·68	2·99	2·73
m	2·34	2·13	2·08	2·13	2·04	2·14
g	2·48	2·73	3·15	2·84	3·02	2·88
b	2·98	2·95	3·33	3·03	3·54	3·07

[a] For description of the parameters listed here and calculation of the most favourable polyhedron see Figure 8a and Ref. 58. For references to the compounds see Table 1.

4 Dimensions of Nitrato-groups

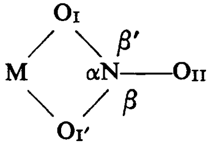
In a regular environment the nitrate ion is known to be planar with all ONO interbond angles equal to 120°. A range of values has been quoted for the length of the N–O bonds, although recent accurate determinations[61] generally agree on a value of 1·245 ± 0·01 Å. In all the different types of co-ordinated nitrate group thus far identified the planarity of the nitrate ion is preserved and this plane generally includes the metal ion. However, the N–O bond lengths and ONO

[61] E. Grison, K. Eriks, and J. L. de Vries, *Acta Cryst.*, 1950, **3**, 290; R. M. Curtis and R. A. Pasternak, *Acta Cryst.*, 1955, **8**, 675; A. J. Serewicz, B. K. Robertson, and E. A. Meyers, *J. Phys. Chem.*, 1965, **69**, 1915; P. Cherin, W. C. Hamilton, and B. Post, *Acta Cryst.*, 1967, **23**, 455, and references therein.

interbond angles are generally found to be different from the values in the nitrate ion.

A. Symmetrically Bidentate Nitrato-groups.—The average values for the dimensions of symmetrically bidentate nitrato-groups that have been obtained to a high degree of accuracy (N–O bond lengths to within ± 0·02 Å and ONO interbond angles to within ± 1°) are listed in Table 6. Two important features are seen immediately. Firstly, in every instance the terminal N–O bond is shorter, and the N–O bonds involving the co-ordinated oxygens are longer than the N–O bonds in the nitrate ion. Secondly, the ONO interbond angle involving both co-ordinated oxygen atoms is less than 120° and the other two angles are correspondingly increased. These changes in the length of the N–O bonds have been noted previously[50] for a more limited number of compounds. Figure 9 shows that N–O bond length changes smoothly with bond order, but the relationship is not a linear one. The sensitivity of N–O bond lengths to co-ordination of the nitrate group is not surprising, since the N–O bonds concerned are in the region of the curve in Figure 9 where the length is very susceptible to changes in the (valence) bond order. However, on co-ordination the overall (valence) bond order of the N–O bonds of the nitrate groups is preserved (Table 7) in agreement with the model of metal–nitrate interaction suggested by Hester and Grossman.[62]

Table 6 *Dimensions of symmetrically bidentate nitrato-groups in Å and degrees*



Compound	Average values							
	$M–O_I$	$M–O_{I'}$	$N–O_I$	$N–O_{I'}$	$N–O_{II}$	α	β	β'
$Ti(NO_3)_4$	2·06	2·08	1·30	1·29	1·19	111	125	125
$(Ph_4As)[Fe(NO_3)_4]$	2·13	2·14	1·27	1·27	1·22	114	123	123
$Co(NO_3)_3$	1·89	1·90	1·28	1·29	1·19	110	124	126
$Cu(NO_3)(Ph_3P)_2$	2·22	2·22	1·25	1·25	1·16	118	121	121
$Sn(NO_3)_4$	2·15	2·18	1·29	1·29	1·18	112	124	124
$La(NO_3)_3bipy_2$*	2·59	2·61	1·24	1·24	1·20	117	121	121
$Mg_3[Ce(NO_3)_6]_2.24H_2O$	2·61	2·65	1·26	1·26	1·22	117	122	122
$(NH_4)_2[Ce(NO_3)_6]$	2·49	2·51	1·28	1·27	1·21	115	124	122
$Th(NO_3)_4(H_2O)_3.2H_2O$	2·54	2·60	1·27	1·26	1·20	115	123	122
$Rb[UO_2(NO_3)_3]$	2·48	2·48	1·26	1·26	1·21	118	121	121
$UO_2(NO_3)_2(H_2O)_2.4H_2O$	2·53	2·53	1·27	1·27	1·22	115	122	122

None of the bond lengths have been corrected for the effect of libration. Only examples having e.s.d.'s of less than 0·02 Å and 1° are included. For references see Table 1.
*We are indebted to Dr. J. S. Wood for making these results available.

It is interesting to note that the changes in both the N–O bond lengths and

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[62] R. E. Hester and W. E. L. Grossman, *Inorg. Chem.*, 1966, **5**, 1308.

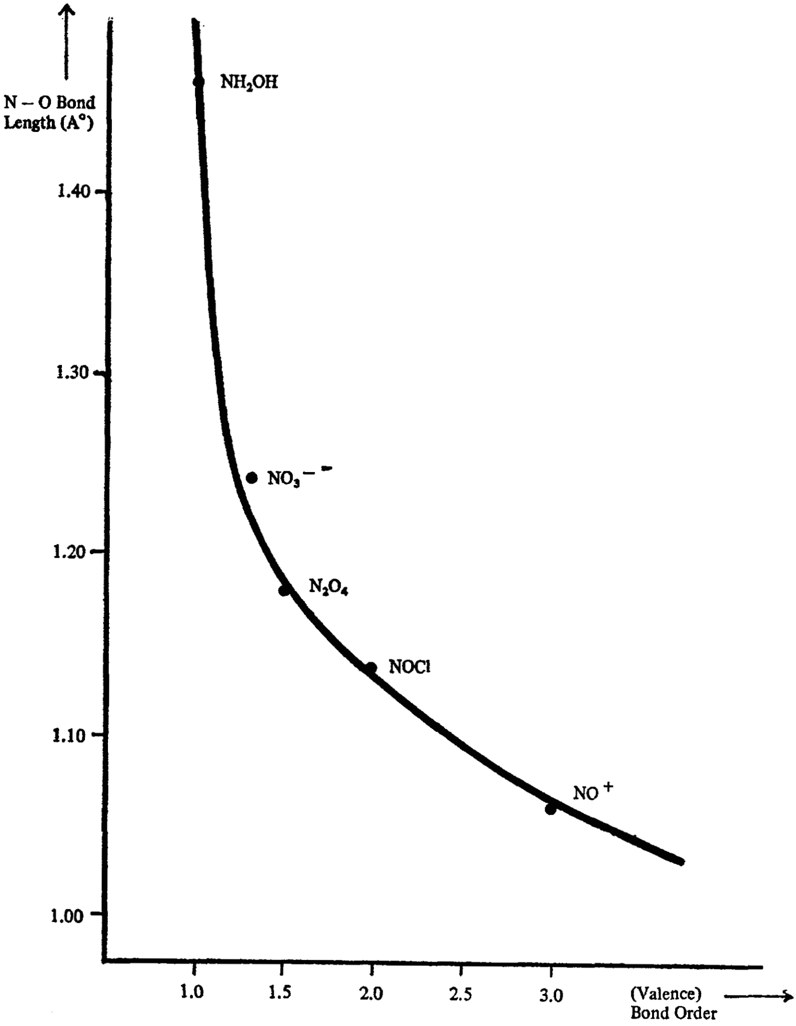

Figure 9 *Variation of* N–O *bond length with* (*valence*) *bond order*

ONO interbond angles of these symmetrically bidentate nitrato-groups correlate reasonably well with the 'polarising power' (measured as charge/radius) of the various cations involved (Figures 10 and 11), $Cu(NO_3)(Ph_3P)_2$[63] in Figure 10 being a notable exception. The contraction of the ONO interbond angle, which involves both the co-ordinated oxygen atoms, might be considered a con-

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[63] G. G. Mesmer and G. J. Palenik, *Inorg. Chem.*, 1969, **8**, 2750.

Table 7 *Total (valence) bond orders* of symmetrically bidentate nitrato-groups*

Compound	*Average Value*
$Ti(NO_3)_4$	4·0
$(Ph_4As)[Fe(NO_3)_4]$	3·8
$Co(NO_3)_3$	4·0
$Cu(NO_3)(Ph_3P)_2$	3·9
$Sn(NO_3)_4$	4·0
$La(NO_3)_3bipy_2$	3·9
$Mg_3[Ce(NO_3)_6].24H_2O$	3·9
$(NH_4)_2[Ce(NO_3)_6]$	3·9
$Th(NO_3)_4(H_2O)_3.2H_2O$	3·9
$Rb[UO_2(NO_3)_2(H_2O)_2].4H_2O$	3·9
free NO_3^-	4·0

*These values have been calculated using the data listed in Table 6 together with the information contained in Figure 9.

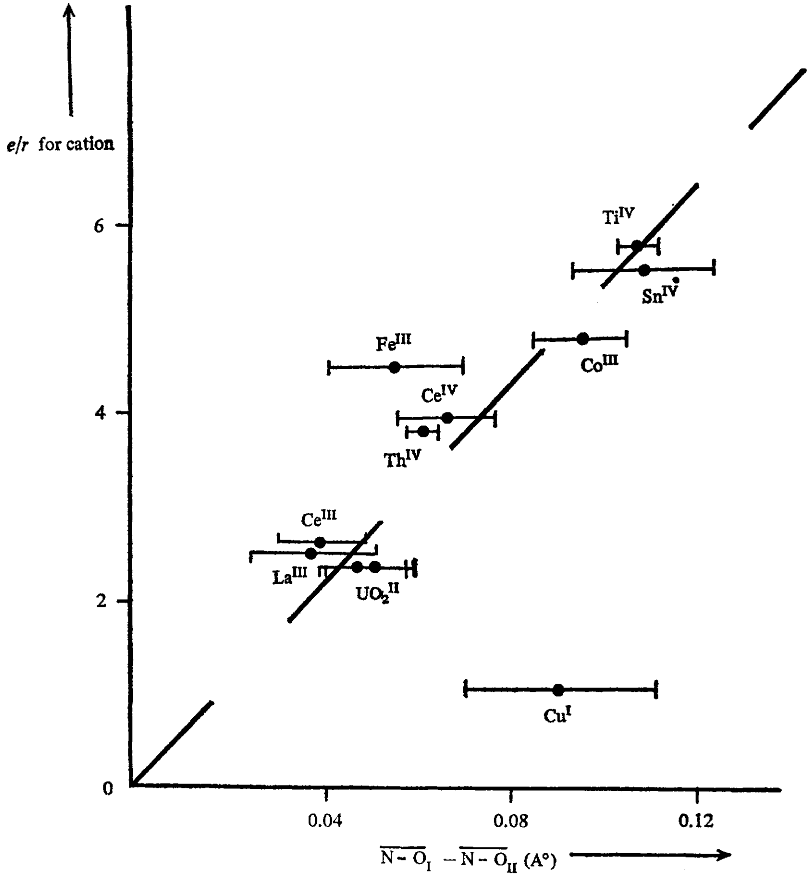

Figure 10 *Variation of the difference in the length of the* N–O *bonds of symmetrically bidentate nitrato-groups with the 'polarising power' of the metal cation. (The cationic radii are taken from reference 20 and the* N–O *bond lengths from Table 6)*

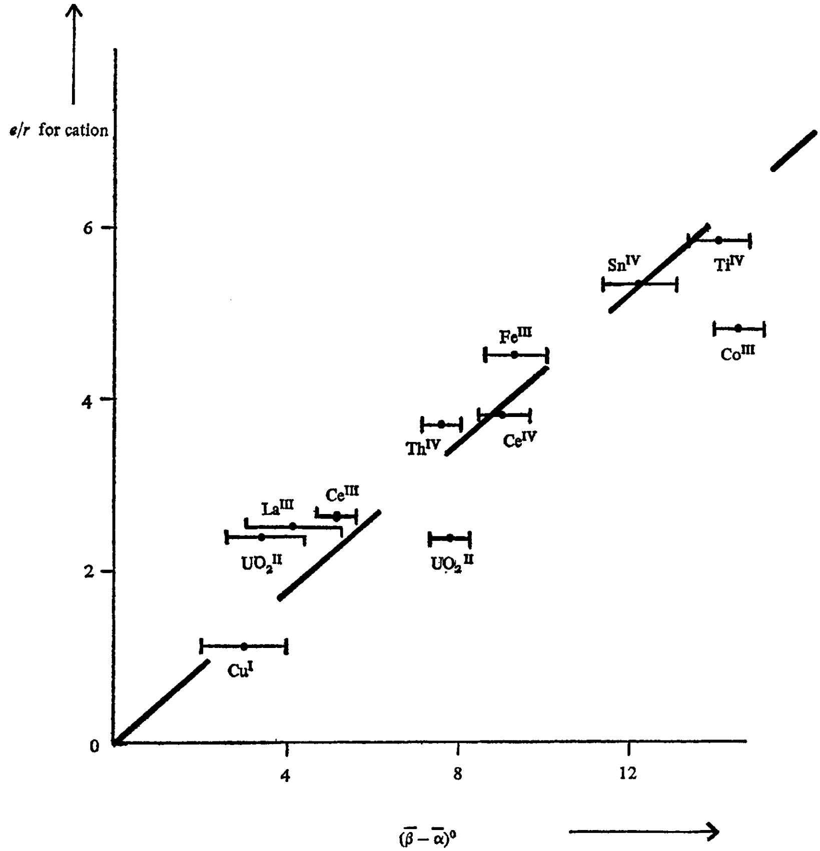

Figure 11 *Variation of the difference in the* ONO *interbond angles of symmetrically bidentate nitrato-groups with the 'polarising power' of the metal cation. (The cationic radii are taken from reference 20 and the* ONO *interbond angles from Table 6)*

sequence of the attraction of the electron clouds of these atoms by the metal cation. However, since the ONO interbond angle involving both co-ordinated oxygens is also reduced for bridging nitrato-groups (Table 8), where the attraction would tend to increase this angle, that explanation seems unlikely. An alternative interpretation, consistent with the above facts, appears to be provided by the valence-shell electron-pair-repulsion model of inorganic stereochemistry.[64] As the electron pairs in the N–O bonds, involving the co-ordinated oxygen atoms, are polarised towards the oxygen atoms, so the repulsion between these electron pairs is diminished and thus the angle subtended at the nitrogen is

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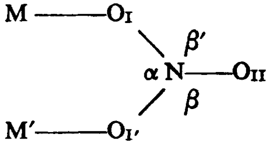
[64] R. J. Gillespie and R. S. Nyholm, *Quart. Revs.*, 1957, **11**, 339.

Table 8 *Dimensions of bridging nitrato-groups in Å and degrees (together with their e.s.d.'s, where published)*



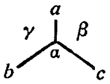
Compound	M–O$_\text{I}$	M′–O$_{\text{I}'}$	N–O$_\text{I}$	N–O$_{\text{I}'}$	N–O$_\text{II}$	α	β	β′
$Cu(NO_3)_2$ (average values)	1·94	1·94	1·31	1·31	1·17	112	124	124
	3	3	4	4	4			
$Cu(NO_3)_2$	2·02	2·02	1·33	1·23	1·16	114	122	124
	3	3	4	4	4			
$Cu(NO_3)_2(MeCN)_2$	2·02	2·31	1·35	1·21	1·21	114	130	115
	4	4	8	5	5	5	7	6
$Cu(NO_3)_2(MeNO_2)$	1·94	1·96	1·29	1·25	1·23	116	127	117
	2	2	3	3	3			
$Zn(NO_3)_2(H_2O)_2$	2·10	2·22	1·23	1·22	1·24	121	122	118
$Cu(NO_3)_2(H_2O)_2 \cdot \frac{1}{2}H_2O$	1·978	2·391	1·306	1·235	1·222	117·0	124·6	118·3
	2	2	3	3	3	0·1	0·1	0·1

For references see Table 4.

reduced. Since the ONO interbond angles are not all equal to 120°, the hybridisation of the σ-orbitals of the nitrogen no longer constitutes three equivalent sp^2 hybrids. The bond angles observed indicate† that the σ-N–O bonds involving the co-ordinated oxygen atoms have more nitrogen *p*-character than sp^2, whilst that involving the terminal oxygen atom has correspondingly less, *e.g.* in $Co(NO_3)_3$ the nitrogen σ-orbitals are hybridised as two $s^{\frac{1}{4}}p^{\frac{3}{4}}$ and one $s^{\frac{1}{2}}p^{\frac{1}{2}}$.

The observed changes in the length of the N–O bonds can be attributed to modifications of both the σ- and π-bonding of the nitrate group on co-ordination. The effect of the rehybridisation of the nitrogen σ-orbitals discussed above is expected to lead to changes in the length of the N–O bonds in the sense observed.[66] However, it is unlikely[67] that this is the sole cause since, not only do the

†For the case of a planar molecule



then the hybridisation ratio, λ, in a hybrid orbital of the form $s + \lambda p_\sigma$ is

$$\lambda_a = \left[\frac{-\cos a}{\cos \beta \cos \gamma}\right]^{\frac{1}{2}}$$

and similarly for λ_b and λ_c.[65]

These equations mean that as the ONO angle opposite a particular bond increases then the amount of *p*-character in the nitrogen σ-orbital involved in that bond increases. The covalent radius of nitrogen is expected to vary with hybridisation as $r_{sp^3} > r_{sp^2} > r_{sp}$.[66] Hence the longest σ–N–O bond is predicted to be opposite the largest ONO interbond angle, and *vice-versa.*

[65] C. A. Coulson, V. Henri Memorial Volume, Desoer, Liége, 1948, p. 15.

[66] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, 1959, **5**, 166.

[67] R. S. Mulliken, *ibid.*, 1959, **6**, 68.

observed changes in the bond lengths appear to be too great, but also the effect of co-ordination on the π-bonding within the nitrato-group is expected to affect the bond lengths in the same manner. This is readily appreciated, since the valence bond structure A, Figure 12, will make a greater contribution to the

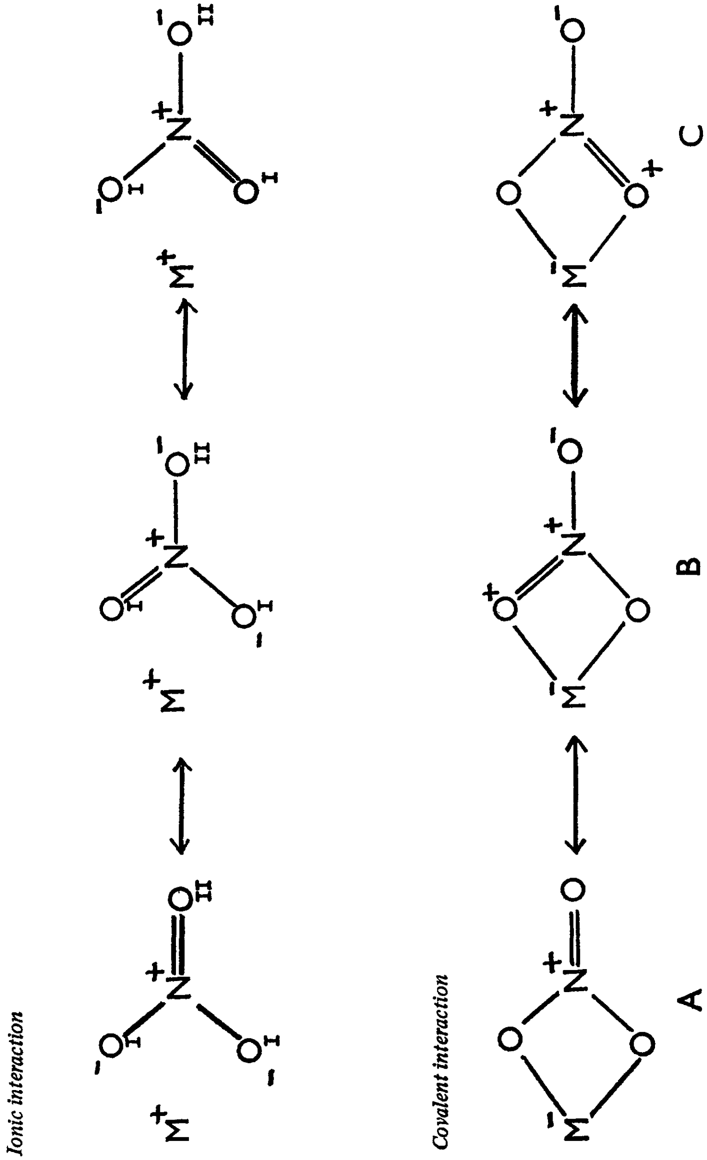


Figure 12 *Valence bond structures for symmetrically bidentate nitrato-groups*

resonance structure of the molecule than will the other two structures B and C. A completely equivalent description of the changes in π-bonding may be presented using molecular orbital theory.

Thus the changes in dimensions of the nitrate group when it co-ordinates as a symmetrically bidentate ligand can be understood both qualitatively, and to some extent quantitatively, even if the metal–nitrate interaction is considered to be ionic in character. On the other hand, covalent bonding between the metal and the nitrate group will also explain the changes in dimensions, as shown in the lower half of Figure 12. There can be little doubt about the importance of covalency in nitrato-complexes such as $Ti(NO_3)_4$, $Co(NO_3)_3$, and $Sn(NO_3)_4$, which are readily sublimable *in vacuo* and are soluble in a non-polar solvent such as carbon tetrachloride. There is less certainty about the relative importance of covalence and polarisation phenomena in compounds such as $(Me_3PO)_2Co(NO_3)_2$ and $(NH_4)_2[Ce(NO_3)_6]$.

B. Bridging Nitrato-groups.—The dimensions obtained so far for bridging nitrato-groups are listed in Table 8, together with their estimated standard deviations. The uncertainty in the dimensions precludes much discussion. However, the general variations in the length of the N–O bonds and in the magnitude of the ONO interbond angles resemble those described for symmetrically bidentate nitrato-groups. Similar arguments to those presented for the latter may be used to explain the nature of these variations.

C. Unidentate Nitrato-groups.—The structures so far determined involving unidentate nitrato-groups all show this group to have C_s symmetry with a MON angle generally in the range of 110—120° at the co-ordinated oxygen. Table 9 presents the more accurate dimensions obtained for unidentate nitrato-groups, together with their estimated standard deviations, where published. It is seen from these data that the perturbations of the unidentate nitrato-groups are generally similar. The ONO interbond angle (β) opposite the co-ordinated oxygen atom is seen to be greater than 120° and the other two angles (α, β') are generally less than 120°, usually with $\alpha > \beta'$. It is not clear why α should be greater than β' since the electron-pair-repulsion model of stereochemistry discussed above would predict $\alpha < \beta' < \beta$. The observed relative magnitudes of the ONO interbond angles indicate[65,66] that, in terms of the hybridisation of the nitrogen σ-orbitals, the N–O bond lengths should be $N–O_{II'} < N–O_{II} < N–O_I$. However, consideration of the changes in π-bonding that occur when a nitrate group co-ordinates as a unidentate ligand (Figure 13) would lead to the predicted order $N–O_{II} < N–O_{II'} < N–O_I$ (a weak interaction[31] over the $M \cdots\cdots O_{II'}$ distance being expected from the position of $O_{II'}$). Inspection of Table 9 shows that the N–O bond involving the co-ordinated oxygen atom (O_I) is longer, and those involving the other two oxygen atoms (O_{II}, $O_{II'}$) are generally shorter, than the N–O bonds of the nitrate ion. Further, the small differences in the lengths of the $N–O_{II}$ and $N–O_{II'}$ bonds are nearly always in the sense expected from π-bonding rather than from σ-bonding considerations, perhaps indicating that

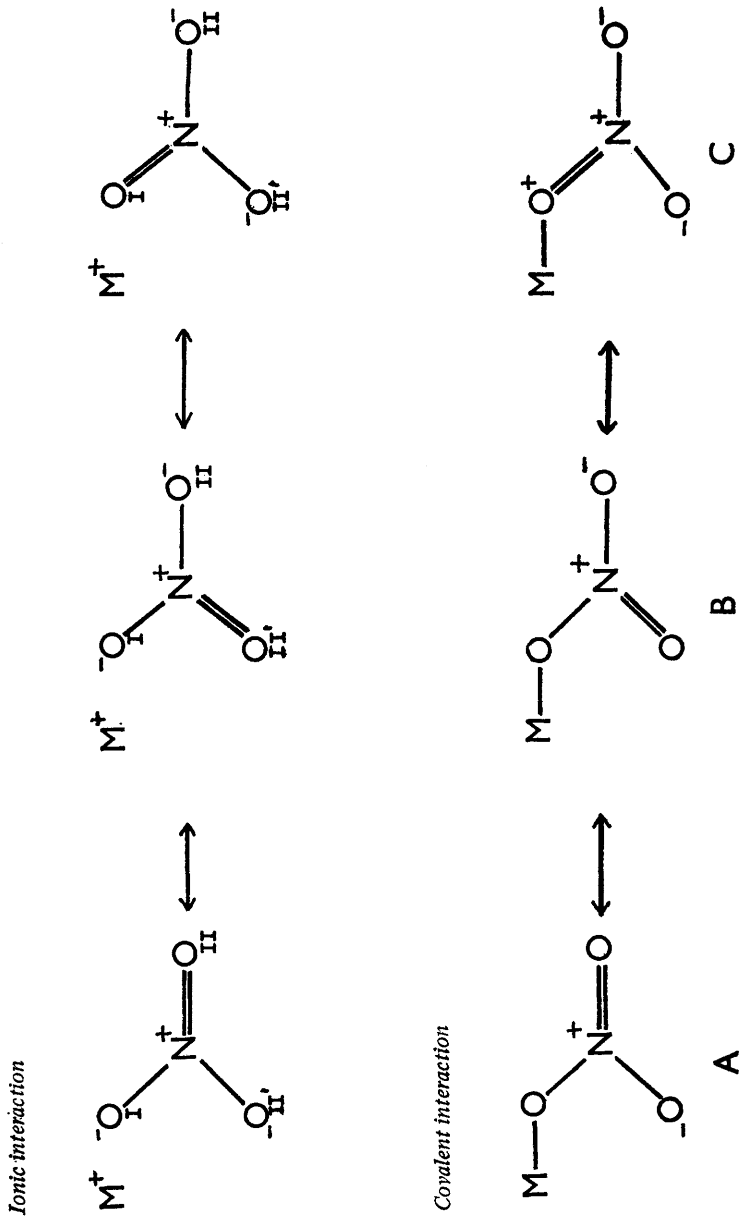
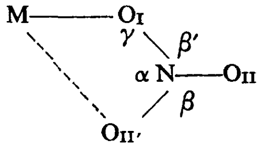


Figure 13 *Valence-bond structures for unidentate nitrato-groups*

changes in π-bonding have the greater effect on the N–O bond lengths in nitrato-complexes generally.

Table 9 *Dimensions of unidentate nitrato-groups in Å and degrees (together with their e.s.d.'s, where published)*



Compound	$\mathrm{M{-}O_{I}}$	$\mathrm{M{-}O_{II'}}$	$\mathrm{N{-}O_{I}}$	$\mathrm{N{-}O_{II'}}$	$\mathrm{N{-}O_{II}}$	α	β	β'	γ
$\mathrm{Ni(NO_3)_2(H_2O)_4}$	2·08	3·10	1·29	1·24	1·21	118	124	119	125
	1	1	1	1	1				
$\mathrm{Ni(NO_3)_2(H_2O)_4}$	2·05	2·90	1·30	1·24	1·26	121	121	118	122
	1	1	1	1	1				
$\mathrm{Cu(NO_3)_2}$ (pyridine	1·97	2·80	1·32	1·23	1·22	119·5	123·1	117·3	112·8
N-oxide)$_2$	1	1	1	1	1	0·5	0·5	0·5	0·5
$\mathrm{Cu(NO_3)_2}$ (pyridine	1·97	2·75	1·30	1·22	1·23	117·9	125·6	116·4	113·2
N-oxide)$_2$	1	1	1	1	1	0·5	0·5	0·5	0·5
$\mathrm{Cu(NO_3)_2}$(1,4-di-	2·36	3·09	1·26	1·22	1·21	120	122	119	119
azacyclohep-	1	1	1	1	1	1	1	1	1
tane)$_2$.½$\mathrm{H_2O}$									
$\mathrm{K[Au(NO_3)_4]}$	2·02	2·85	1·34	1·24	1·14	118	129	114	114
	2	2	2	3	3	2	2	2	2
$\mathrm{K[Au(NO_3)_4]}$	1·99	2·87	1·39	1·22	1·20	118	131	112	114
	1	2	3	3	2	2	2	2	1
$\mathrm{HNO_3}$[j]	0·96	2·14	1·41	1·21	1·20	116	130	114	102
	1	1	1	1	1				
Pentaerythritol[k]	1·46	2·54	1·40	1·23	1·20	117	130	113	113
tetranitrate	1	1	1	1	1	1	1	1	1

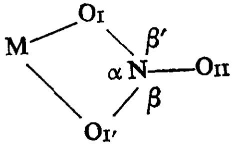
Unidentate nitrato-groups have also been identified in several other compounds. However, sufficient information has not been published for these to be included.

References as for Table 3, plus [j] A. P. Cox and J. M. Riveros, *J. Chem. Phys.*, 1965, **42,** 3106; [k] J. Trotter, *Acta Cryst.*, 1963, **16**, 698.

D. Unsymmetrically Bidentate Nitrato-groups.—Table 10 shows the information presently available concerning the dimensions of unsymmetrically bidentate nitrato-groups which, like unidentate nitrato-groups, have C_s symmetry. The limited number of examples together with the relatively large estimated standard deviations, mean that no definite conclusions can be drawn. However, as one might expect, the observed variations in the lengths of the N–O bonds and the magnitudes of the ONO interbond angles generally resemble those obtained for unidentate nitrato-groups.

Thus, the changes in the dimensions of nitrato-groups that occur on co-ordination appear to be systematically related to the mode of co-ordination and, for symmetrically bidentate nitrato-groups, to the particular cation involved. These data therefore provide evidence of the effect of these two factors on the nature of the nitrate ligand. It is thus of interest to discuss certain physical and chemical properties of nitrato-groups in the light of the above structural data.

Table 10 *Dimensions of unsymmetrically bidentate nitrato-groups in Å and degrees (together with their e.s.d.'s, where published)*



Compound	M–O$_I$	M–O$_{I'}$	N–O$_I$	N–O$_{I'}$	N–O$_{II}$	α	β	β'
$(Ph_4As)_2[Co(NO_3)_4]$	2·03	2·36	1·25	1·20	1·20	110	128	122
	2	2	2	3	3	2	2	2
$(Ph_4As)_2[Co(NO_3)_4]$	2·11	2·54	1·25	1·21	1·24	117	128	115
	2	2	2	3	3	2	2	2
$Cu(NO_3)_2(MeCN)_2$	1·89	2·50	1·31	1·30	1·23	107	130	122
	4	4	5	7	5	4	5	5
$Cu(NO_3)_2$ (pyrazine)	2·010	2·490	1·287	1·249	1·214	116·7	124·0	119·3
	4	5	7	7	7	0·5	0·6	0·5
$Cu(NO_3)_2(H_2O)_2.\frac{1}{2}H_2O$	1·992	2·653	1·281	1·238	1·241	118·6	122·1	119·2
	2	2	3	3	3	0·1	0·1	0·1
$Me_2Sn(NO_3)_2$	2·11	2·38	1·29	1·33	1·18	108	125	126
$Me_2Sn(NO_3)_2$	2·12	2·65	1·34	1·20	1·28	124	120	116

For references see Table 2.

5 Vibrational Spectra of Nitrate Groups

Much attention has been paid to the vibrational spectra of the nitrate group. Early work was concerned with the problem of distinguishing between ionic and co-ordinated nitrate groups.[68] This is readily achieved since the nitrate ion exhibits absorptions in the i.r. at *ca.* 1390, 830, and 720 cm^{-1} and in the Raman at *ca.* 1390, 1050, and 720 cm^{-1}, whereas co-ordinated nitrate groups give rise to six bands in both i.r. and Raman spectra.

However, to distinguish between the various types of co-ordinated nitrate groups, a more detailed analysis of the spectra is required. A considerable amount of work has been concerned with such analyses and as a result several means of identifying the mode of co-ordination of nitrate groups have been proposed. In particular:

(i) the number of bands exhibited in the far i.r. region;[69,70]
(ii) the positions of the two highest frequency N–O stretching vibrations;[4,71]
(iii) the depolarisation ratios of the three highest N–O stretching vibrations in the Raman spectrum;[72,73]
(iv) the sequence of relative intensities of the three highest frequency Raman shifts attributable to nitrate fundamentals.[74,75]

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[68] B. M. Gatehouse, S. E. Livingstone and R. S. Nyholm, *J. Chem. Soc.*, 1957, 4222.
[69] G. Topping, *Spectrochim. Acta*, 1965, **21**, 1743.
[70] R. H. Nuttall and D. W. Taylor, *Chem. Comm.*, 1968, 1417.
[71] N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, 1965, **4**, 804.
[72] J. R. Ferraro, A. Walker, and C. Cristallini, *Inorg. Nuclear Chem. Letters*, 1965, **1**, 25.
[73] C. C. Addison, D. W. Amos, D. Sutton, and W. H. H. Hoyle, *J. Chem. Soc.* (*A*), 1967, 808.
[74] D. W. Amos, Ph.D. Thesis, Nottingham, 1967.
[75] C. C. Addison, D. W. Amos, G. S. Brownlee, N. Logan, and A. Morris, to be published.

In view of the current interest in this problem it is worthwhile attempting to assess the predictive value of these criteria by considering their application to nitrato-complexes whose structures have been determined. Attention must, however, be drawn to two features common to all these criteria which may limit their general applicability. Firstly, the model used in each case involves only one nitrato-group bonded to a metal. Hence, at the outset, all coupling between nitrato-groups (and other ligands) is neglected. Secondly, the majority of these studies have been restricted to a distinction between symmetrically bidentate nitrato-groups on the one hand and unidentate nitrato-groups on the other. Whilst these do appear to be the two common modes of nitrate co-ordination, we have seen that the nitrate group is a surprisingly versatile ligand.

(i) Since a bidentate nitrato-group involves two metal–oxygen bonds whereas a unidentate group involves only one, it has been suggested[69,70] that bidentate nitrato-groups should exhibit two metal–oxygen frequencies whereas unidentate nitrato-groups should only exhibit one. However, it has been pointed out[76] that this model is a gross over-simplification since it ignores the vibrational coupling mentioned above which is expected to be extensive in such low frequency vibrations. Furthermore, a recent normal co-ordinate treatment[74] of the bidentate nitrato-group has led to the prediction that the symmetric metal–oxygen stretch might lead to absorptions at frequencies as high as 800 cm^{-1} due to mixing effects within the small MO_2NO chelate ring. Thus the far-i.r. spectra of complexes containing nitrato-groups are seldom as simple[76,77] as criterion (i) would suggest.

(ii) Normal co-ordinate calculations[62,78] have been carried out for symmetrically bidentate and unidentate (both C_{2v} and C_s) nitrato-groups in order to indicate the probable changes in frequency which would result, in theory, from an increase in the polarisation of the nitrate ion by the metal ion, and/or an increase in the metal–oxygen covalent bonding (Figure 14). The trends in the N–O force constants calculated for both symmetrically bidentate and unidentate bonding modes are qualitatively consistent with the observed lengths of the N–O bonds in such groups. For symmetrically bidentate co-ordination the calculations[62] predict that the order of the N–O stretching vibrations will be

(N–O_{II} stretching) A_1 > (N–O_I antisymmetric stretching) B_1 >

(N–O_{II} + symmetric N–O_I stretching) A_1.

Whilst for unidentate co-ordination (C_{2v}) the expected order is[78,79]

(N–O_{II} antisymmetric stretching) B_1 > (N–O_I + symmetric N–O_{II} stretching)

A_1 > (N–O_I stretching) A_1.

Distinction between symmetrically bidentate and unidentate nitrato-groups on

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[76] J. I. Bullock and F. W. Parrett, *Chem. Comm.*, 1969, 157.
[77] A. Walker and J. R. Ferraro, *J. Chem. Phys.*, 1965, **42**, 1273, 1278; 1965, **43**, 2689.
[78] H. Brintzinger and R. E. Hester, *Inorg. Chem.*, 1966, **5**, 980.
[79] G. S. Brownlee, Ph.D. Thesis, Nottingham, 1969.

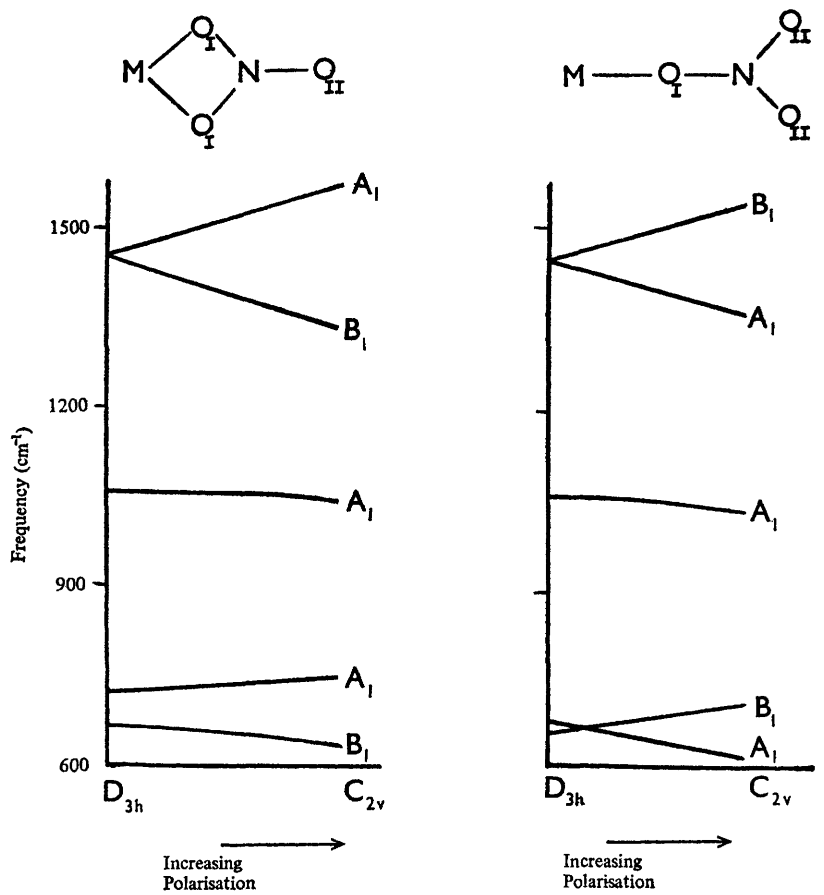

Figure 14 *Frequency shifts in symmetrically bidentate and unidentate* (C_{2v}) *nitrato-groups as the degree of polarisation increases, with a fixed metal–nitrate covalent interaction* (M–O_I *force constants* 1·0 md Å^{-1} *throughout*)
(These diagrams have been adapted from references 62 and 78)

the basis of criterion (ii) requires the separation of the two highest frequency bands to be characteristic of the mode of co-ordination, symmetrically bidentate attachment giving rise to a greater separation than unidentate co-ordination.[71] In addition, Field and Hardy[4] have suggested that the occurrence of two strong bands, one at a frequency greater than 1570 cm^{-1} and the other at a frequency of less than 1280 cm^{-1} might indicate the presence of bridging nitrato-groups. Clearly, however, the nature of the metal cation and the other ligands co-ordinated to it will also influence the positions of these two bands and it is not surprising that a wide range of frequencies is observed for symmetrically bidentate, unidentate, and bridging nitrato-groups (Table 11). Distinction between

Table 11 N–O *stretching frequencies in some nitrates of established structure*

Compound	N–O *stretching frequencies* (cm^{-1})			*Mode of bonding*[i]
$Sn(NO_3)_4$	1629	1250	973[a]	Symmetrically bidentate
$Ti(NO_3)_4$	1635	1225	993[a]	„
$K[UO_2(NO_3)_3]$	1555 1521	1271	1025[b]	„
$Th(NO_3)_4(H_2O)_3.2H_2O$	1502	1322 1295	1030[c]	„
$[Mg(H_2O)_6]_3[Ce(NO_3)_6]_2.6H_2O$	1440	1330	1040[d]	„
$(Ph_4As)_2[Co(NO_3)_4]$	1525	1335	1042[e]	Unsymmetrically bidentate
	1486	1287	1025	
$K[Au(NO_3)_4]$	1570	1286	920[f]	Unidentate
HNO_3	1710	1320	886[g]	„
$Cu(NO_3)_2MeNO_2$	1519	1291	1008[h]	Bridging
$Cu(NO_3)_2$	1510			„
	1502	1300	1049[h]	
	1478		1015	
	1435			

[a] Ref. 73; [b] J. G. Allpress and A. N. Hambly, *Aust. J. Chem.*, 1959, **12**, 569; [c] J. R. Ferraro, *J. Mol. Spectroscopy*, 1960, 4, 99; [d] C. C. Addison, D. W. Amos, and D. Sutton, unpublished results; [e] R. J. Fereday and D. Sutton, *Chem. Comm.*, 1966, 510; [f] C. C. Addison, G. S. Brownlee, and N. Logan, to be published; [g] H. Cohn, C. K. Ingold, and H. G. Poole, *J. Chem. Soc.*, 1952, 4272; [h] N. Logan and W. B. Simpson, *Spectrochim. Acta*, 1965, **21**, 857; [i] For references to the diffraction studies see Tables 1, 2, 3, and 4.

nitrato-groups on the above basis must therefore be made with caution.[51] However, it does appear that if the vibrational spectrum of a nitrate group co-ordinated to a metal atom has its highest frequency band at *ca.* 1600 cm^{-1} and is separated by *ca.* 350 cm^{-1} from the next highest frequency band, then co-ordination as a symmetrically bidentate or bridging ligand is likely.

(iii) This criterion relies on the fact that A_1 and B_1 vibrational modes may be distinguished in the Raman spectrum since the former is Raman polarised, whereas the latter is Raman depolarised. Table 12 gives the sequence of the polarisations of the three highest frequency (N–O stretching) Raman bands expected[62,78] for symmetrically bidentate and unidentate‡ nitrato-groups (see Figure 14), together with the results of some studies on compounds which contain these groups. It is seen that there is good agreement between the predicted and observed sequences and hence this technique would appear to offer a convenient means of distinguishing between unidentate and symmetrically bidentate nitrato-groups. However, it must be noted that coupling between nitrato-groups may lead to complications. The normal co-ordinate calculations[62,78] mentioned

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‡Although these arguments have been developed assuming C_{2v} symmetry for unidentate nitrato-groups, the conclusions for C_s are basically the same.[78]

Table 12 *Predicted and observed sequence of polarisations of the three highest-frequency Raman bands exhibited by nitrato-groups*

Increasing frequency ←

Compound	*Structure*[f]		*Band*		
			1	2	3
	Unidentate C_{2v}	Predicted[a]	B_1 (dp)	A_1 (p)	A_1 (p)
HNO_3	,, C_s	Observed[b]	dp	p	p
CH_3NO_3	,, C_s	Observed[c]	dp	p	p
	Symmetrically bidentate C_{2v}	Predicted[d]	A_1 (p)	B_1 (dp)	A_1 (p)
$Ti(NO_3)_4$	,, ,,	Observed[e]	p	dp	p
$Sn(NO_3)_4$	,, ,,	Observed[e]	p	dp	p

p = polarised; dp = depolarised.

[a] Ref. 78; [b] G. E. McGraw, D. L. Bernitt, and I. C. Hisatsune, *J. Chem. Phys.*, 1965, **42,** 237; [c] J. C. D. Brand and T. M. Cawthon, *J. Amer. Chem. Soc.*, 1955, **77**, 319; [d] Ref. 62; [e] Ref. 73; [f] For references to diffraction studies see Tables 1 and 3.

above made use of idealised models (of C_{2v} and C_s symmetry) whereas in *e.g.* $Ti(NO_3)_4$, the molecular symmetry[16] approaches D_{2d} and as a result of intramolecular vibrational coupling, three bands transforming as $A_1 + B_2 + E$ would be expected in each region of N–O stretching. All components are allowed in the Raman effect, with only A_1 polarised. The model calculations[62,78] only anticipated a single band in each N–O stretching region and criterion (iii) cannot therefore apply rigorously to polynitrato-species. Nevertheless, the simpler approach in terms of the C_{2v} (and C_s) models has proved to be reasonably successful and several authors have, with some justification, inferred bidentate[72,73,80] or unidentate[81] co-ordination from Raman polarisation data.

It is not expected that this method will allow a distinction between symmetrically bidentate and bridging nitrato-groups since the pattern of depolarisation ratios should be identical. It will, however, be of interest to observe the pattern of depolarisation ratios obtained for unsymmetrically bidentate nitrato-groups as they are intermediate in nature between symmetrically bidentate and unidentate groups.

(iv) The recent accumulation of Raman data for nitrato-species has brought to light a further feature of nitrate spectra, first noted by Amos,[74] which appears to provide a reliable distinction between the unidentate and symmetrically bidentate modes of co-ordination. This is to be found in the sequence of relative intensities of the three highest-frequency Raman shifts attributable to nitrate fundamentals. The sequence for unidentate species differs from that for symmetrically bidentate species and the data assembled in Table 13 for nitrates of known structure illustrate the nature of this distinction. In summary, it is found

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[80] J. R. Ferraro, C. Cristallini, and I. Fox, *J. Inorg. Nuclear Chem.*, 1967, **29,** 139.

[81] P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, 1962, **58,** 1495; R. E. Hester and R. A. Plane, *J. Chem. Phys.*, 1964, **40,** 411; R. E. Hester, R. A. Plane, and G. E. Walrafen, *J. Chem. Phys.*, 1963, **38,** 249.

Table 13 *Relative Raman intensities for* N–O *stretching bands in various nitrato-species of known structure*

Increasing frequency
←

Compound	*Band* 1	2	3	*Structure*[f]
HNO_3	w	vs	s[a]	Unidentate
CH_3NO_3	s	vs	w[b]	,,
$[Au(NO_3)_4]^-$	w	s	s[c]	,,
$Ti(NO_3)_4$	vs	w	m[d]	Symmetrically bidentate
$Sn(NO_3)_4$	vs	w	m[d]	,, ,,
$[Ce(NO_3)_6]^{2-}$	s	w	s[c]	,, ,,
$[Fe(NO_3)_4]^-$	s	w	s[e]	,, ,,
$[Mn(NO_3)_4]^{2-}$	m	w	vs[e]	,, ,,

vs = very strong, s = strong, m = medium, w = weak. For typical frequency ranges see Table 11.

[a] G. E. McGraw, D. L. Bernitt, and I. C. Hisatsune, *J. Chem. Phys.*, 1965, **42**, 237; [b] J. C. D. Brand and T. M. Cawthon, *J. Amer. Chem. Soc.*, 1955, **77**, 319; [c] Ref. 79; [d] Ref. 74; [e] Ref. 18; [f] For references to diffraction studies see Tables 1 and 3.

that for unidentate nitrato-complexes, band 2 ($N–O_I + N–O_{II}$ symmetric stretch) is generally fairly strong, and is by no means the least intense of the three bands. In contrast, for symmetrically bidentate species, band 2 (now the $N–O_I$ antisymmetric stretch) is weak and without exception the least intense of the three bands.

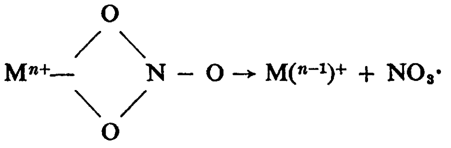
This differing intensity sequence may be rationalised by consideration of the electron shifts which occur on co-ordination of the nitrate ion, since it is known that the intensity of a Raman band is related semi-quantitatively to the order of the bond(s) being stretched in the normal co-ordinate. For bidentate co-ordination the structural data suggest an increase of electron density in the terminal ($N–O_{II}$) bond, and a corresponding decrease in the electron density in the other two ($N–O_I$) bonds, relative to the situation in the nitrate ion. This, together with a consideration of the above assignments of the bands, allows a qualitative understanding of the observed relative intensities. Further, the more polarising the cation, the closer the terminal ($N–O_{II}$) bond approaches a double bond and thus the greater the expected intensity of the highest frequency band. It is of interest to note that the observed trend in the intensity of this band is consistent with the relative magnitudes of the polarising power of the cations suggested by the N–O bond length data (Figure 10). For unidentate co-ordination the observed relative intensities do not appear to correlate so readily with the structural data. Nevertheless, it is possible to understand the high intensity of band 2 since the vibrational mode responsible for this involves a considerable amount of terminal ($N–O_{II}$) symmetric stretching and it is the terminal bonds that are shortened in unidentate co-ordination.

It therefore appears that the relative intensities of the three highest-frequency

Raman shifts, together with their depolarisation ratios, currently provide the most acceptable means of distinguishing between the two extremes of unidentate and symmetrically bidentate co-ordination of the nitrate group to metals.

6 Chemical Reactivity of Nitrato-groups

The oxidising powers of nitrato-groups vary widely.[82,83,84] Thus, $Sn(NO_3)_4$ and $Ti(NO_3)_4$ explode or inflame with organic solvents such as ethers, and the former oxidises aliphatic hydrocarbons immediately on contact,[84] whereas compounds such as $Cs[UO_2(NO_3)_3]$, $(Ph_4As)_2[Co(NO_3)_4]$, and $K[Au(NO_3)_4]$ are relatively inert. The reactivity of the nitrate is clearly determined by the nature of the metal–nitrate bond and those compounds which possess strong oxidising properties have been shown (either by diffraction or Raman studies) to contain strongly co-ordinated symmetrically bidentate nitrato-groups. In addition, it is observed that the marked reactivity is only obtained with nitrates of metals for which a lower oxidation state is readily available.[82] These and other experimental results are consistent[83] with a mechanism which involves the release of $NO_3\cdot$ radicals, species which are known to be capable of such reactivity. An attractive scheme for this radical release is the fission of a metal–nitrate three-centred bond as



This may well be a representation of the transition state, particularly if the reaction proceeds by an S_N2 mechanism, since it clearly allows the metal to acquire an additional ligand whilst remaining co-ordinated to the nitrate group. It may appear surprising that the complexes which involve the most strongly co-ordinated nitrate groups are reactive. However, only when the nitrate group is strongly co-ordinated will bond fission be homolytic and $NO_3\cdot$ radicals be formed.

Investigations which aim to achieve a better understanding of the remarkable chemistry exhibited by many of these nitrato-complexes are currently in progress.[85]

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[82] C. C. Addison, C. D. Garner, W. B. Simpson, D. Sutton, and S. C. Wallwork, *Proc. Chem. Soc.*, 1964, 367.

[83] C. C. Addison, *Coord. Chem. Revs.*, 1966, **1**, 588.

[84] C. C. Addison and W. B. Simpson, *J. Chem. Soc.*, 1965, 598.

[85] C. C. Addison, M. I. Khalil, and N. Logan, unpublished results.