Unidentate *versus* Symmetrically and Unsymmetrically Bidentate Nitrate Co-ordination in Pyrazole-containing Chelates. The Crystal and Molecular Structures of (Nitrato-*O*)[tris(3,5-dimethylpyrazol-1-ylmethyl)amine]copper(II) Nitrate, (Nitrato-*O,O'*)[tris(3,5-dimethylpyrazol-1-ylmethyl)amine]nickel(II) Nitrate, and (Nitrato-*O*)(nitrato-*O,O'*)[tris(3,5-dimethylpyrazol-1-ylmethyl)-amine]cadmium(II)†

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The crystal structures of three compounds $ML(NO_3)_2$ are described, where M = Cu, Ni, or Cd and L is the tripodal quadridentate ligand tris(3,5-dimethylpyrazol-1-ylmethyl)amine. The structure of the copper compound can best be described as tetragonally distorted trigonal bipyramidal. As in the other compounds, the ligand L utilizes each of its four potential donor sites. One nitrate ion is unidentate, yielding a CuN_4O chromophore. In the nickel compound a nitrate ion is symmetrically bidentate, yielding a distorted octahedral *cis*-NiN_4O_2 chromophore. In the cadmium compound one of the nitrate ions is unsymmetrically bidentate, the other symmetrically bidentate, yielding a CdN_4O_3 chromophore. The structure is best described as distorted bicapped octahedral. The nitrate co-ordination modes were investigated using several spectroscopic techniques. Criteria to differentiate between the unidentate, unsymmetrically bidentate, and symmetrically bidentate modes are presented. In this type of compound discrimination between the co-ordination modes solely on the basis of spectroscopic behaviour appears not to be possible. Slight changes in the i.r. spectra of $CuL(NO_3)_2$, and of the analogous cobalt and zinc compounds, upon applying pressure can be understood in terms of changes in the nitrate co-ordination.

Recently a novel synthetic route towards pyrazole-containing ligand systems has been reported.[1] One of the first ligands prepared in this way was tris(3,5-dimethylpyrazol-1-ylmethyl)-amine (abbreviated as L, see Figure 1). The synthesis and spectroscopic properties of chelates containing this ligand, as well as the crystal structure of the dimer $[Co_2F(H_2O)(C_2H_5OH)L_2][BF_4]_3\cdot1.5C_2H_5OH$, have been described recently.[2]

In this paper the crystal structures and electronic spectra of the compounds $[CuL(ONO_2)]NO_3$, (1), $[NiL(O_2NO)]NO_3$, (2), and $[CdL(O_2NO)(ONO_2)]$, (3), are described. The i.r., electronic, and e.s.r. properties of the analogous zinc and cobalt compounds as well as of the copper-doped zinc and cadmium compounds were also investigated, in order to obtain insight into the co-ordination of nitrate ions in these compounds.

Nitrate ions are reported[3–9] to adopt unidentate, symmetrically bidentate, or unsymmetrically bidentate (anisobidentate) modes when bonded to transition-metal ions. Methods to discriminate between uni- and bi-dentate nitrate ions have been reported and have often proved reliable (see ref. 10, for instance). They are based on the pattern of the $\nu_1 + \nu_4$ combination bands[11] or on the splitting of ν_3.[12,13] In the present investigation the region near 1 750 cm^{-1} was used, as there are no other absorptions present in the $\nu_1 + \nu_4$ region. Thus a less ambiguous assignment of the observed bands is possible.

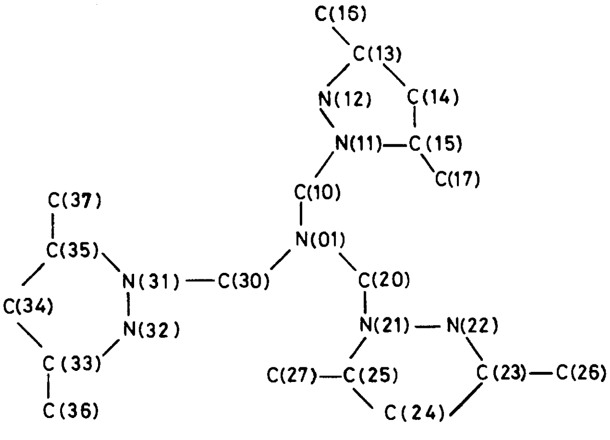

Figure 1. Numbering for the ligand L

The main reason to undertake an in-depth investigation of the spectroscopic properties of the L-containing nitrate chelates was the observation that the i.r. spectra of the compounds in the 1 750 cm^{-1} region were slightly different for the various metals, and in some cases changed upon pressing a KBr disc. These changes pointed towards a change in the co-ordination mode of the nitrate ion.[11] Electronic reflectance and e.s.r. spectra were recorded to confirm the observed changes, and to obtain information about their nature. If a change is observed in the nitrate $\nu_1 + \nu_4$ region in the i.r. spectrum and if the electronic diffuse reflectance and e.s.r. of the pure compound and of its powdered KBr pellet differ as well, it may be concluded that something has changed in the co-ordination sphere.

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† *Supplementary data available* (No. SUP 56290, 5 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Crystallographic data and details of data collection and processing for $ML(NO_3)_2$, with M = Cu [in (**1**)], Ni [in (**2**)], and Cd [in (**3**)]

	(**1**)	(**2**)	(**3**)
Stoicheiometry	$C_{18}H_{27}CuN_9O_6$	$C_{18}H_{27}N_9NiO_6$	$C_{18}H_{27}CdN_9O_6$
M	529.01	524.18	577.88
Lattice type	Monoclinic	Triclinic	Orthorhombic
Space group	*I*2/*c*	*P* −1	*Pbca*
a/Å	23.376(6)	7.843(2)	12.218(8)
b/Å	10.548(3)	10.910(3)	20.818(3)
c/Å	20.866(5)	14.817(4)	18.574(5)
α/°	90	90.26(2)	90
β/°	108.70(2)	108.03(2)	90
γ/°	90	95.99(2)	90
U/Å^3	4 873.3	1 198.1	4 724.3
Z	8	2	8
D_c/g cm^{-3}	1.44	1.44	1.63
F(000)	2 202.4	548.7	2 336.0
μ(Mo-K_α)/cm^{-1}	9.45	8.56	9.71
Approximate crystal dimensions (mm)	0.52 × 0.40 × 0.23	0.45 × 0.20 × 0.10	0.56 × 0.30 × 0.14
Number of setting angles	12	24	25
θ range/° (cell dimensions)	$-10.24 < \theta < -11.77$	$10.15 < \theta < 11.83$	$9.61 < \theta < 12.02$
(data collection)	$2 < \theta < 22$	$2 < \theta < 25$	$0 < \theta < 24$
h range	$-24 < h < 24$	$-9 < h < 9$	$0 < h < 14$
k range	$0 < k < 11$	$-13 < k < 13$	$0 < k < 23$
l range	$-22 < l < 22$	$-17 < l < 17$	$-21 < l < 21$
Number of reflections:			
measured	6 349	8 415	7 456
independent	3 176	4 256	3 695
observed	2 303	2 700	3 099
Final *R*	0.0392	0.0588	0.031
Final *R'*	0.0509	0.0756	—

Experimental

Preparations.—The preparation of the cobalt, nickel, copper, and zinc nitrate complexes with ligand L has been described elsewhere.[2] The copper-doped zinc and cadmium compounds were prepared similarly. Single crystals of compound (**3**) were obtained by adding a solution of L (0.002 mol) in methanol to a solution of $Cd(NO_3)_2$ (0.002 mol) in methanol. After *ca.* 4 h needle-like single crystals could be isolated (Found: C, 37.5; H, 5.00; Cd, 19.25; N, 21.7. $C_{16}H_{27}CdN_9O_6$ requires C, 37.4; H, 4.70; Cd, 19.45; N, 21.8%).

Crystallography.—Crystal data and details of the data collection and data processing are listed in Table 1.

The cell dimensions of the single crystals were determined from the measured setting angles of a number of reflections (Table 1) by least-squares refinement. *X*-Ray intensities were collected on four-circle Enraf–Nonius CAD4 diffractometers (at Leiden and at Nijmegen) at room temperature, using graphite-monochromatized Mo-K_α radiation (λ = 0.710 73 Å). The ω—θ scan technique was applied. Lorentz and polarization corrections were applied; corrections for absorption were made only in the case of compound (**3**).[14,15]

Structure analysis and refinement. The observed reflections were used to solve the structures by heavy-atom and Fourier techniques. The structures were refined by full-matrix least-squares methods, with anisotropic thermal parameters for all non-hydrogen atoms.

For compound (1), Waser constraints were applied for the non-co-ordinating nitrate ion, and the thermal parameters of all hydrogen atoms were fixed at $B = 3.94$ Å^2. The refinement yielded a final *R* of 0.0392 ($R' = 0.0509$). For compound (**2**), Waser constraints were applied for the non-co-ordinating nitrate species as well. Due to disorder, two different orientations with different occupancies were required. Though one of these orientations still appeared to be disordered, no attempt was made to specify another orientation. Hydrogen atoms were assigned C–H distances of 1.0 Å and constant thermal parameters of $B = 3.65$ Å^2. A final value for *R* of 0.0588 ($R' = 0.0756$) was obtained.

The structure of compound (**3**) was solved by DIRDIF,[16] with the heavy-atom position, automatically located with the SHELX 84 [17] Patterson option, as input. All non-hydrogen atoms were found as the 34 peaks with highest intensity. The SHELX[18] program was used for structure refinement. Fixed thermal parameters were used for the hydrogen atoms ($B = 4.74$ Å^2), and carbon–hydrogen distances were constrained. Using unit weights, a final *R* of 0.031 was obtained for 388 parameters and 3 099 'observed' reflections. Reflections with $|F_o| < 3\sigma(F_o)$ were omitted from the least-squares refinement.

Refinements were considered complete when the shift-to-error ratio of each parameter was less than 0.35. The function minimized was $\Sigma w(||F_o| - |F_c||)^2$ with $w = 1/\sigma^2(F_o)$. The conventional discrepancy index was defined as $R = \Sigma(||F_c| - |F_o||)/\Sigma|F_o|$ and the weighted factor as $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. Scattering factors and anomalous dispersion corrections were taken from ref. 19.

The atomic co-ordinates of the non-hydrogen atoms are listed in Table 2, selected bond lengths in Table 3, and selected bond angles in Table 4.

Physical Properties.—Infrared spectra in the range 4 000—300 cm^{-1} for samples mulled in Nujol between KRS5 discs, or pelleted in KBr, were recorded on a Perkin-Elmer 580 spectrophotometer, equipped with a data station. Electronic reflectance spectra in the range 28 000—5 000 cm^{-1} were recorded on a Perkin-Elmer 330 spectrophotometer, also equipped with a data station, using MgO as reference. E.s.r. spectra were recorded on a Varian E-3 spectrophotometer (*X*-band frequencies) at room temperature and at 77 K (liquid nitrogen).

Table 2. Atomic co-ordinates with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
(*a*) Compound (**1**) ($\times 10^5$ for Cu, $\times 10^4$ for others)							
Cu	7 734(2)	11 519(5)	62 931(2)	C(27)	2 251(3)	671(8)	4 844(4)
N(01)	1 493(1)	−122(3)	6 454(2)	C(30)	2 044(2)	483(5)	6 905(2)
C(10)	1 359(2)	−1 289(5)	6 758(3)	N(31)	1 888(1)	1 149(3)	7 431(2)
N(11)	708(1)	−1 425(3)	6 566(2)	N(32)	1 386(1)	1 906(3)	7 246(2)
N(12)	379(1)	−356(3)	6 561(2)	C(33)	1 395(2)	2 512(4)	7 809(2)
C(13)	−162(2)	−764(4)	6 558(2)	C(34)	1 907(2)	2 157(5)	8 332(2)
C(14)	−171(2)	−2 078(4)	6 570(2)	C(35)	2 220(2)	1 302(4)	8 094(2)
C(15)	386(2)	−2 475(4)	6 586(2)	C(36)	918(3)	3 421(6)	7 819(3)
C(16)	−651(2)	142(7)	6 546(4)	C(37)	2 788(2)	622(6)	8 412(3)
C(17)	650(3)	−3 767(5)	6 606(4)	N(40)	−304(2)	2 265(5)	5 590(3)
C(20)	1 549(2)	−339(5)	5 777(2)	O(41)	136(1)	2 399(3)	6 163(2)
N(21)	1 509(2)	902(3)	5 458(2)	O(42)	−717(2)	3 031(5)	5 486(3)
N(22)	1 099(1)	1 738(3)	5 555(2)	O(43)	−272(2)	1 385(5)	5 217(2)
C(23)	1 123(2)	2 745(4)	5 177(2)	N(50)	1 960(2)	3 011(5)	3 346(2)
C(24)	1 539(3)	2 539(6)	4 854(2)	O(51)	1 968(2)	4 072(5)	3 604(3)
C(25)	1 786(2)	1 358(5)	5 035(2)	O(52)	1 526(2)	2 345(6)	3 201(2)
C(26)	743(3)	3 859(6)	5 139(3)	O(53)	2 417(2)	2 613(5)	3 337(4)
(*b*) Compound (**2**) ($\times 10^4$)							
Ni	5 110(1)	3 357(1)	7 658(1)	N(31)	2 270(6)	1 531(4)	7 437(3)
N(01)	4 516(6)	1 860(4)	6 658(3)	N(32)	2 763(6)	2 672(4)	7 868(3)
C(10)	5 885(9)	995(6)	7 036(5)	C(33)	1 964(8)	2 706(6)	8 528(4)
N(11)	6 173(6)	936(4)	8 049(4)	C(34)	897(8)	1 577(7)	8 516(5)
N(12)	6 420(6)	2 047(5)	8 549(3)	C(35)	1 109(8)	827(6)	7 812(4)
C(13)	6 802(8)	1 740(7)	9 452(5)	C(36)	2 223(9)	3 805(7)	9 165(5)
C(14)	6 818(11)	476(8)	9 522(6)	C(37)	326(10)	−423(6)	7 459(6)
C(15)	6 405(9)	−15(6)	8 625(5)	N(40)	7 521(8)	5 107(5)	8 260(4)
C(16)	7 092(10)	2 741(8)	10 200(5)	O(41)	6 084(6)	4 914(4)	8 518(3)
C(17)	6 208(11)	−1 311(6)	8 281(6)	O(42)	8 610(7)	5 982(5)	8 553(4)
C(20)	4 684(10)	2 395(6)	5 790(5)	O(43)	7 666(5)	4 302(4)	7 690(3)
N(21)	3 777(7)	3 513(5)	5 656(4)	N(50A)	1 902(9)	8 557(6)	5 048(5)
N(22)	3 928(6)	4 195(5)	6 453(4)	O(51A)	1 307(7)	7 942(6)	4 339(5)
C(23)	2 971(9)	5 137(6)	6 121(6)	O(52A)	3 333(10)	8 780(8)	5 620(7)
C(24)	2 311(10)	5 059(8)	5 134(6)	O(53A)	573(14)	8 512(6)	5 431(6)
C(25)	2 805(9)	3 985(7)	4 857(5)	N(50B)	2 032(9)	8 882(6)	4 874(5)
C(26)	2 759(11)	6 060(7)	6 797(6)	O(51B)	1 353(7)	8 323(6)	4 169(5)
C(27)	2 488(11)	3 386(8)	3 912(5)	O(52B)	3 281(10)	9 440(8)	5 053(7)
C(30)	2 652(8)	1 313(6)	6 551(4)	O(53B)	1 492(14)	8 544(6)	5 645(6)
(*c*) Compound (**3**) ($\times 10^5$ for Cd, $\times 10^4$ for others)							
Cd	21 921(2)	64 256(1)	54 356(2)	C(27)	4 894(5)	5 291(3)	3 498(3)
N(01)	4 035(3)	6 788(1)	4 922(2)	C(30)	3 744(4)	7 156(2)	4 276(2)
C(10)	4 490(4)	7 199(2)	5 487(2)	N(31)	3 012(3)	6 766(2)	3 842(2)
N(11)	4 428(3)	6 849(2)	6 167(2)	N(32)	2 145(3)	6 468(2)	4 164(2)
N(12)	3 482(3)	6 531(2)	6 338(2)	C(33)	1 634(4)	6 147(2)	3 634(2)
C(13)	3 698(3)	6 241(2)	6 962(2)	C(34)	2 167(4)	6 253(2)	2 981(2)
C(14)	4 763(4)	6 378(2)	7 190(2)	C(35)	3 039(3)	6 645(2)	3 124(2)
C(15)	5 216(3)	6 764(2)	6 673(2)	C(36)	677(4)	5 730(3)	3 783(3)
C(16)	2 853(4)	5 817(2)	7 296(2)	C(37)	3 869(5)	6 940(3)	2 629(3)
C(17)	6 311(4)	7 069(2)	6 624(3)	N(40)	1 663(3)	7 723(2)	6 084(2)
C(20)	4 709(3)	6 220(2)	4 782(2)	O(41)	1 997(3)	7 561(2)	5 466(2)
N(21)	4 025(3)	5 658(2)	4 643(2)	O(42)	1 657(4)	8 287(2)	6 262(2)
N(22)	3 256(3)	5 483(2)	5 146(2)	O(43)	1 318(3)	7 300(2)	6 494(2)
C(23)	2 858(4)	4 923(2)	4 907(3)	N(50)	0(3)	6 183(2)	5 833(2)
C(24)	3 370(4)	4 748(2)	4 261(3)	O(51)	157(3)	6 541(2)	5 304(2)
C(25)	4 113(4)	5 221(2)	4 105(2)	O(52)	907(3)	6 126(2)	6 107(2)
C(26)	2 003(5)	4 577(3)	5 330(3)	O(53)	824(3)	5 885(2)	6 078(2)

Results and Discussion

Description of the Crystal Structures.—The crystal structures of compounds (**1**)—(**3**) are depicted in Figure 2, and their co-ordination spheres are redrawn in Figure 3. In each compound the ligand utilizes each of its four potential donor sites, thus acting as a tripodal quadridentate ligand. The structures of (**1**) and (**2**) comprise distinct $[ML(NO_3)]^+$ cations and NO_3^- anions. All nitrate species are planar; the same applies to all pyrazole rings. The methyl groups lie in the planes of their parent pyrazole ring within the error range. There is no stacking between the rings in any of the compounds. The packing of the co-ordination units in the crystal lattice proceeds through normal van der Waals contacts.

The structure of compound (**1**) can best be described as tetragonally distorted trigonal bipyramidal, with a CuN_4O chromophore. In an ideal trigonal bipyramid, with atoms N(01)

Table 3. Selected bond lengths (Å) for the compounds $ML(NO_3)_2$, with M = Cu (**1**), Ni (**2**), and Cd (**3**). Estimated standard deviations are given in parentheses. For the atom numbering see Figures 1–3

	(**1**)	(**2**)	(**3**)
M–N(01)	2.094(3)	2.115(5)	2.559(3)
M–N(12)	2.006(3)	2.080(5)	2.311(3)
M–N(22)	2.022(3)	2.011(5)	2.414(4)
M–N(32)	2.193(3)	2.028(5)	2.364(3)
M–O(41)	1.940(3)	2.050(4)	2.377(3)
M–O(43)	2.749(4)	2.143(4)	2.885(4)
N(40)–O(41)	1.311(5)	1.295(7)	1.263(5)
N(40)–O(42)	1.224(5)	1.194(7)	1.219(5)
N(40)–O(43)	1.230(6)	1.254(7)	1.239(5)
M–O(51)	—	—	2.509(3)
M–O(53)	—	—	2.341(3)
N(50)–O(51)	1.239(6)	*	1.247(5)
N(50)–O(52)	1.190(5)	*	1.225(5)
N(50)–O(53)	1.155(6)	*	1.268(5)

* This nitrate ion is disordered.

Table 4. Selected bond angles (°) for $ML(NO_3)_2$ with M = Cu (**1**), Ni (**2**), and Cd (**3**). For the atom numbering see Figures 1—3

	(**1**)	(**2**)	(**3**)
N(01)–M–N(12)	82.2(1)	81.3(2)	69.0(1)
N(01)–M–N(22)	80.7(1)	79.4(2)	71.5(1)
N(01)–M–N(32)	80.2(1)	83.8(2)	68.8(1)
N(01)–M–O(41)	177.1(1)	168.8(2)	78.7(1)
N(01)–M–O(43)	130.3(1)	107.5(2)	113.2(1)
N(01)–M–O(51)	—	—	143.8(1)
N(01)–M–O(53)	—	—	163.7(1)
N(12)–M–N(22)	140.7(1)	159.6(2)	82.6(1)
N(12)–M–N(32)	105.1(1)	98.3(2)	137.5(1)
N(12)–M–O(41)	100.1(1)	100.1(1)	87.6(1)
N(12)–M–O(43)	86.0(1)	90.0(2)	72.5(1)
N(12)–M–O(51)	—	—	137.5(1)
N(12)–M–O(53)	—	—	99.4(1)
N(22)–M–N(32)	106.5(1)	95.1(2)	79.7(1)
N(22)–M–O(41)	98.4(1)	97.6(2)	150.2(1)
N(22)–M–O(43)	78.6(1)	89.5(2)	149.8(1)
N(22)–M–O(51)	—	—	126.1(1)
N(22)–M–O(53)	—	—	96.2(1)
N(32)–M–O(41)	97.5(1)	107.3(2)	98.1(1)
N(32)–M–O(43)	149.2(1)	168.5(2)	130.4(1)
N(32)–M–O(51)	—	—	82.9(1)
N(32)–M–O(53)	—	—	120.6(1)
O(41)–M–O(43)	51.9(1)	61.5(2)	47.1(1)
M–O(41)–N(40)	113.4(3)	93.5(4)	108.7(3)
O(41)–N(40)–O(43)	118.0(4)	114.5(5)	118.6(4)
N(40)–O(43)–M	76.6(3)	90.4(4)	84.5(1)
O(41)–M–O(51)	—	—	78.9(1)
O(41)–M–O(53)	—	—	113.2(1)
O(43)–M–O(51)	—	—	68.9(1)
O(43)–M–O(53)	—	—	72.1(1)
O(51)–M–O(53)	—	—	52.3(1)
M–O(51)–N(50)	—	—	91.1(3)
O(51)–N(50)–O(53)	—	—	116.9(4)
N(50)–O(53)–M	—	—	98.5(2)

and O(41) axial, the N(32)–Cu–N(12) and N(32)–Cu–N(22) angles should be 120°; in an ideal tetragonal pyramid, with atom N(32) at the top, these angles should be 90°. In fact, the angles are almost exactly in between these boundary values, *viz.* 105°. However, because of the small N(12)–Cu–N(22) angle (*ca.* 140°), a description of the structure as trigonal bipyrimidal is preferred [although the Cu–N(32) distance of 2.19 Å clearly indicates a distortion]. Atom O(43) has not been taken into account in the previous description, as the difference between the Cu–O(43) and Cu–O(41) distances is greater than 0.7 Å. This atom is therefore not considered to be co-ordinated to the copper ion.[9]

The structure of compound (**2**) can best be described as distorted octahedral. Here the nitrate ion is co-ordinated in a symmetric bidentate mode, yielding a *cis*-NiN_4O_2 chromophore. The nitrate co-ordination imposes a small O(41)–Ni–O(43) bond angle of about 61.5°.[10,20] As a result, all other octahedral angles show deviations of about 10° from the ideal value of 90°.

The structure of compound (**3**) can either be described as distorted bicapped octahedral, or, less preferably,[9] as distorted octahedral if both atoms O(51) and O(53) are considered to occupy one co-ordination site. The equatorial plane is formed by the atoms N(12), N(22), N(32), and O(41) (root-mean-square distance about 0.1 Å), with the cadmium atom about 0.7 Å out of the plane. This distortion is due to the limited ability of the ligand L to fold around the relatively large cadmium atom, because of the presence of (relatively short) methylene bridges between the central nitrogen atom and the respective pyrazole rings. An oxygen atom of one of the nitrate ions [O(41)] completes this plane. The distances between the cadmium ion and the atoms in this plane vary between 2.3 and 2.4 Å. The Cd–O(53) bond length is of the same order of magnitude, while Cd–O(51) and Cd–N(01) have lengths greater than 2.5 Å. Atom O(43) is considered to be semi-co-ordinating; the nitrate ion to which it belongs co-ordinates in an anisobidentate mode (unsymmetrically bidentate).[5,6,8,21]

Nitrate Co-ordination Modes.—In the three compounds described above no less than four different types of nitrate ions are encountered, *i.e.* ionic, unidentate, symmetrically bidentate, and unsymmetrically bidentate (anisobidentate). Rather rough geometrical criteria to discriminate between the various nitrate co-ordination modes have been published.[9] Comparison of the geometric data for a variety of nitrate species from the literature and the present work enabled refinement of these criteria. Four criteria, expected to be indicative of the degree of symmetry of a co-ordinating nitrate ion, were selected and tested (see Figure 4). In the case of an ideally symmetric bidentate nitrate ion, $l_2 - l_1$ should be 0, $A_1 - A_2$ should be 0, $l_3 - l_2$ should be relatively large, and A_3 should be 180°. In the case of a unidentate nitrate ion, $l_2 - l_1$ and $A_1 - A_2$ will be relatively large, $l_3 - l_2$ will be close to 0, and A_3 will deviate considerably from 180°. The results of the application of these criteria are in Table 5. It can be concluded that the criteria $l_2 - l_1$ and $A_1 - A_2$ yield a distinct and consistent classification of the nitrate ions in three groups. We suggest that the limits in Table 6 be employed to discriminate between the various co-ordination modes.

Spectroscopic Results.—Generally, spectroscopic methods yield valuable information on the detailed co-ordination geometry. In the work described here, i.r., diffuse electronic reflectance, and e.s.r. spectroscopy were used to investigate the co-ordination modes of the nitrate ions.

In the i.r. spectral region the pattern of the $\nu_1 + \nu_4$ combination bands[11] was studied, as these bands are less broad than those of ν_3,[12,13] and as there are no ligand absorptions in this region (near 1 750 cm^{-1}), enabling a less ambiguous assignment. The pattern of the $\nu_1 + \nu_4$ combination bands of the nickel and cobalt compounds is depicted in Figure 5. The values of the $\nu_1 + \nu_4$ splittings for the various compounds are listed in Table 7 (for some other i.r. data, see ref. 2). These values indicate that pressing a KBr pellet affects the nitrate co-ordination in the case of copper, cobalt, and zinc.

In order to confirm the observed changes, and to obtain information about their nature, electronic reflectance and e.s.r. spectra were recorded for some compounds and their powdered

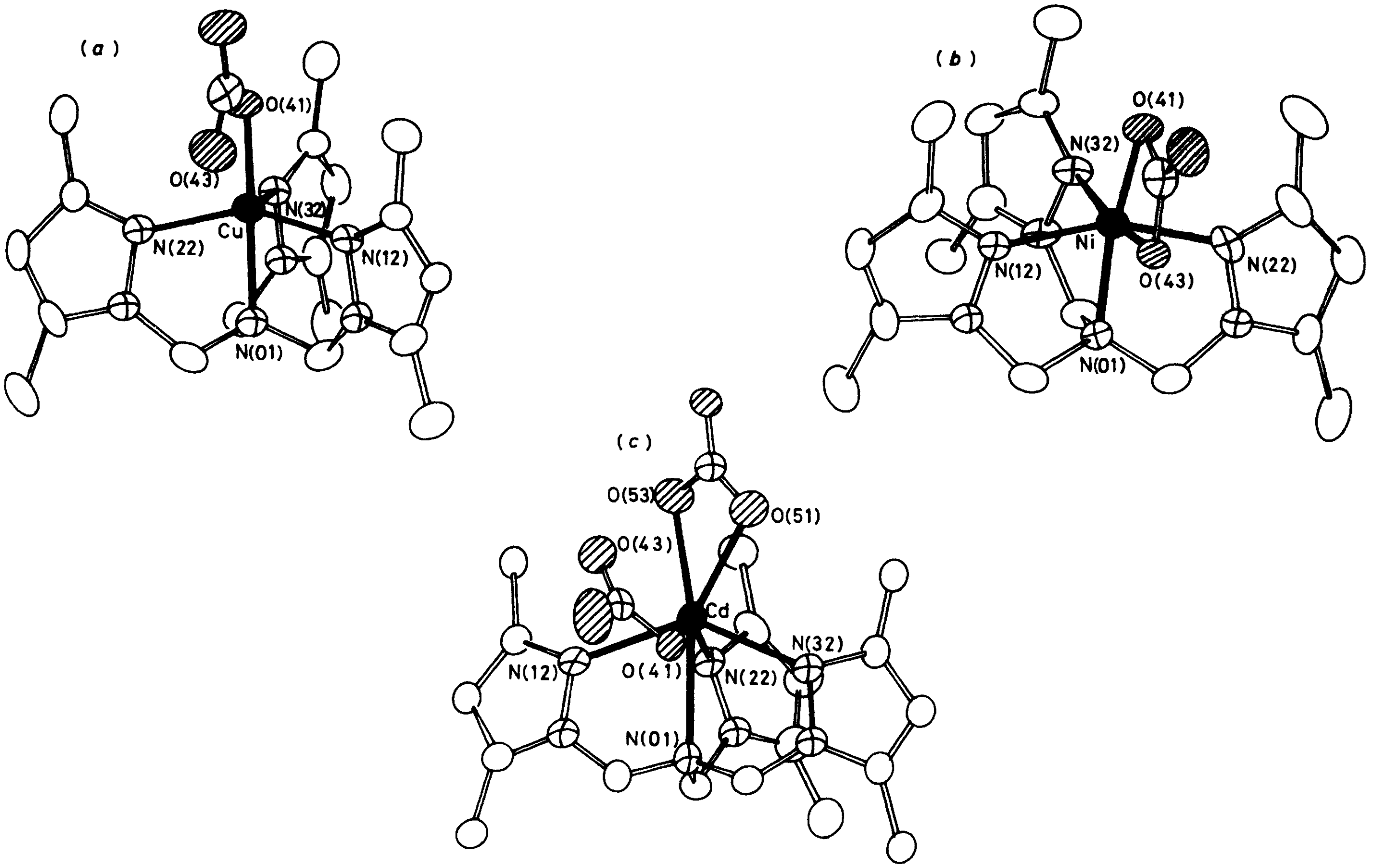

Figure 2. The crystal structures of compounds (**1**) (*a*), (**2**) (*b*), and (**3**) (*c*). Hydrogen atoms and ionic nitrate have been omitted for clarity

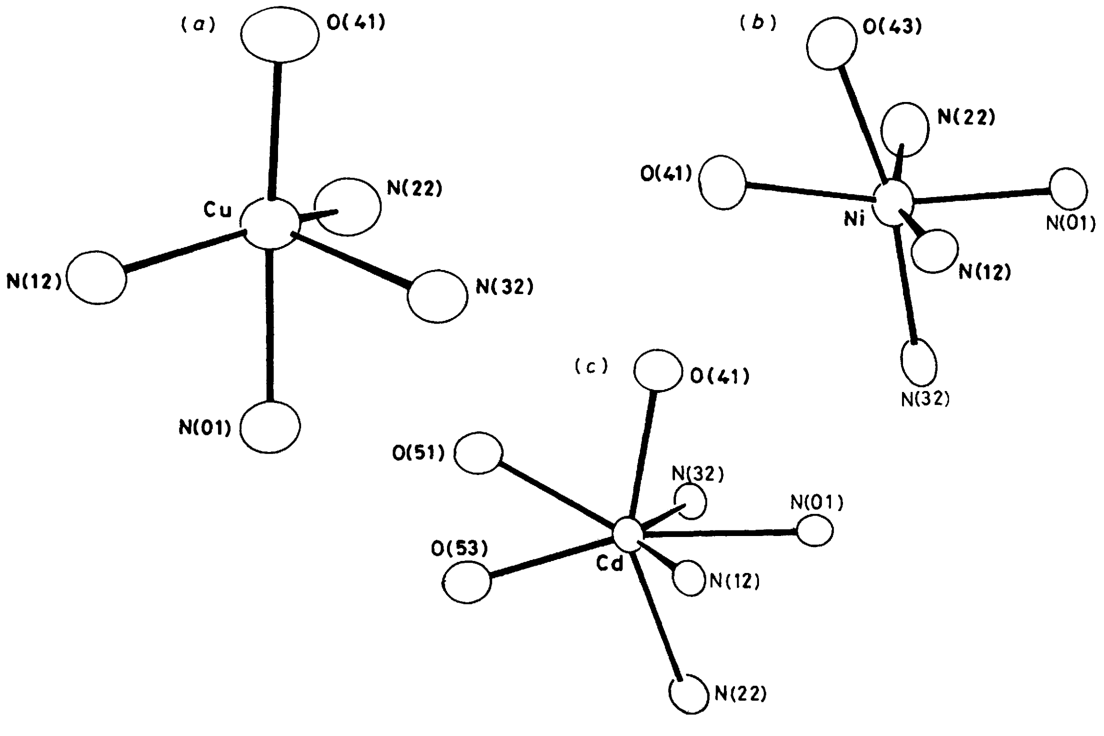

Figure 3. The chromophores of the compounds (**1**) (*a*), (**2**) (*b*), and (**3**) (*c*)

Table 5. Some geometric properties of various co-ordinated nitrates

Metal	Ligand[a]	Ref.[b]	Type[c]	$l_2 - l_1$/Å	$A_1 - A_2$/°	$l_3 - l_2$/Å	A_3/°
Cu	L	*d*	U	0.80	36.8	−0.01	156.4
Cu	tpea	*e*	U	0.71	32.3	0.07	161.2
Ni	bdmpae	20, i	U	0.83	39.8	−0.04	157.1
Cd	L	i[d]	A	0.51	24.2	0.13	165.2
Cu	dmpp	21, i	A	0.46	20.3	0.16	166.4
Cu	dmpp	21, ii	A	0.46	21.0	0.15	163.7
Cu	bipy	5	A	0.53	16.3	0.15	164.4
Cu	Me_4bim	8, i	A	0.39	16.9	0.27	158.9
Ni	L	*d*	B	0.09	3.1	0.35	176.7
Cd	L	ii[d]	B	0.17	7.5	0.31	169.7
Zn	bipy	6	B	0.00	1.2	0.42	—
Zn	Me_4bim	8, ii	B	0.21	9.9	0.24	164.0
Ni	bdmpae	20, ii	B	0.00	0.3	0.32	179.7
Co	PMe_3O	i[f]	B	0.09	4.8	0.26	177.6
Co	PMe_3O	ii[f]	B	0.04	2.1	0.36	178.0

[a] tpea = Tris[2-(2-pyridyl)ethyl]amine; bdmpae = *NN*-bis(3,5-dimethylpyrazol-1-ylmethyl)aminoethane; dmpp = 3,5-dimethyl-1-phenylpyrazole; bipy = 2,2′-bipyridyl; Me_4bim = 4,4′,5,5′-tetramethyl-2,2′-bi-imidazole. [b] If two co-ordinating nitrate groups occur, they are distinguished as i and ii. [c] U = Unidentate, A = anisobidentate, and B = bidentate. [d] This work. [e] K. D. Karlin, P. L. Dahlstrom, J. C. Hayes, R. A. Simon, and J. Zubieta, *Cryst. Struct. Commun.*, 1982, **11**, 907. [f] F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, 1963, **85**, 2402.

Table 6. Criteria to discriminate between the various nitrate co-ordination modes

	Unidentate	Anisobidentate	Bidentate
$l_2 - l_1$/Å	>0.6	0.3—0.6	<0.3
$A_1 - A_2$/°	>28	14—28	<14
$l_3 - l_2$/Å	<0.1	0.1—0.2	>0.2
A_3/°	<162	162—168	>168

Table 7. Δ Values (cm^{-1}) for the $\nu_1 + \nu_4$ splittings in the i.r. spectra of compounds $ML(NO_3)_2$, when recorded as Nujol mulls and as KBr pellets

	Δ	
Metal	Nujol	KBr
Zn	15	50
Cu	33	53
Co	33	52
Cd	35	35
	15	15
Ni	56	56

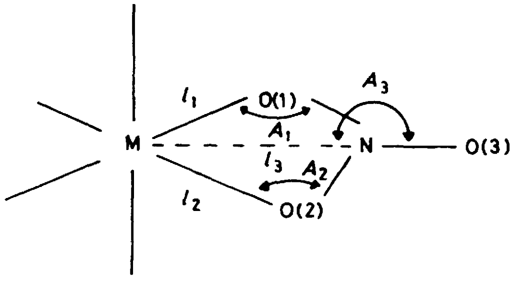

Figure 4. General representation of a co-ordinating nitrate ion (see text)

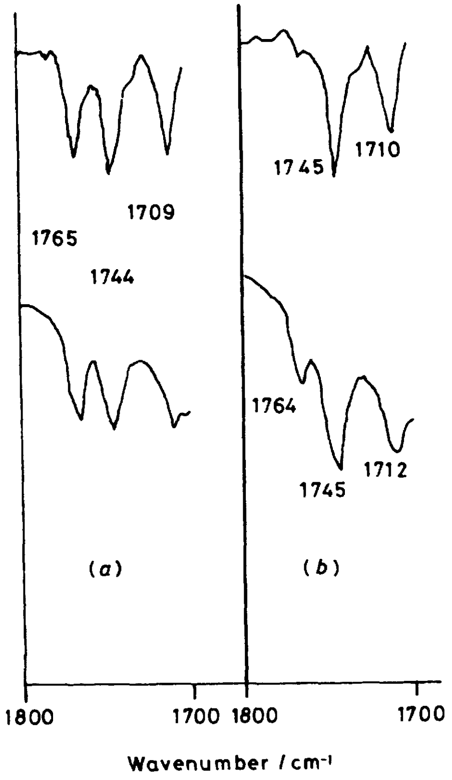

Figure 5. The nitrate $\nu_1 + \nu_4$ overtone region in the i.r. spectra of $NiL(NO_3)_2$ (*a*) and of $CoL(NO_3)_2$ (*b*). At the top the spectra of the compounds mulled in Nujol are depicted; at the bottom, the spectra of the compounds as KBr pellets

KBr pellets (see also ref. 2). In the case of nickel, as expected, no differences were observed between the electronic reflectance spectra of the pure compound and of its powdered KBr pellets (ligand-field bands at 10 200, 17 500, and 27 300 cm^{-1}). The electronic spectra of the copper compound and of its powdered KBr pellet differ slightly. In this case, the main absorption band (11 800 cm^{-1}) is less broad and furthermore a shoulder on the charge-transfer band appears. The difference between the respective e.s.r. spectra are negligible [$g_\perp = 2.11$ (br), $g_\parallel = 2.31$, $A_\parallel = 150 \times 10^{-4}$ cm^{-1}; measured at liquid-nitrogen temperatures]. The same applies for the differences between the e.s.r. spectrum of the 10% copper-doped zinc compound and of its powdered KBr pellet ($g_1 = 2.29$, $A_\parallel = 145 \times 10^{-4}$ cm^{-1}, $g_2 = 2.12$, $g_3 = 2.04$; measured at liquid-nitrogen temperatures). No relevant changes were observed in the e.s.r. spectrum of the 1% copper-doped cadmium compound

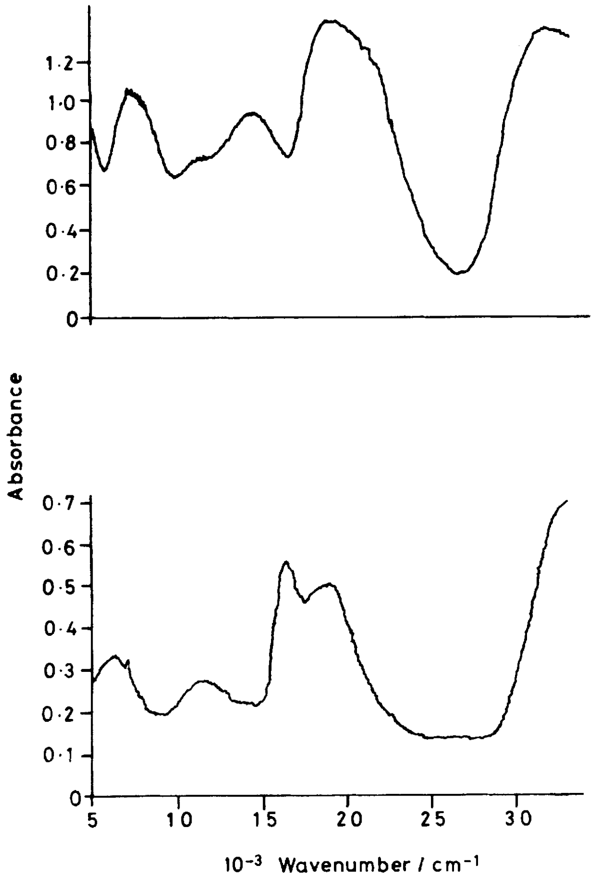

Figure 6. Diffuse reflectance spectra of CoL(NO_3)$_2$ (top) and of its powdered KBr pellet (bottom)

upon pressing a KBr pellet ($g_{\parallel} = 2.28$, $A_{\parallel} = 122 \times 10^{-4}$ cm^{-1}, $g_{\perp} = 2.08$; measured at liquid-nitrogen temperatures).

The most significant changes are observed for CoL(NO_3)$_2$. The electronic reflectance spectra of this compound [ligand-field bands at 7 900, 11 600 (sh), 15 000, and 19 600 cm^{-1}] and of its powdered KBr pellet [6 200, 11 500, 14 000 (sh), 16 500, and 18 700 cm^{-1}] are depicted in Figure 6. Comparison of these spectra shows that changes in the co-ordination geometry do occur upon pressing a KBr pellet. These changes yield a differently distorted five-co-ordination of the metal atom.

Conclusions

Clearly, the changes observed in the region around 1 750 cm^{-1} in the i.r. spectra of some of the nitrate compounds have something to do with the mode of co-ordination of the nitrate ions. As was shown by the crystal structure determination, in the copper compound (**1**), and therefore also in the isomorphous zinc and cobalt compounds, the nitrate is co-ordinated in a unidentate mode. Atom O(43) is at the 'open' side of the (distorted) trigonal bipyramid, at a distance of about 2.75 Å from the copper atom. We suppose that upon exposure to a high pressure the structure becomes slightly compressed, such that atom O(43) moves somewhat closer towards the copper atom.

In the nickel compound (**2**), the nitrate ion is already co-ordinated in a (symmetrically) bidentate mode. Exertion of pressure is not expected to impose drastic changes upon the co-ordination geometry, in accordance with the observation that no changes occur in the spectra. The same applies for the cadmium compound with regard to the symmetrically bidentate co-ordinated nitrate. In contrast, the anisobidentate co-ordinated nitrate ion might be sensitive to high pressure. However, there are some differences with the nitrate ion in compound (**1**). The environment of the cadmium ion is much more compact than that of the copper ion in compound (**1**). There are already seven donor atoms, which leaves no 'open' side as was the case in the trigonal bipyramid (with only five donor atoms) of compound (**1**). The nitrate ion is already, albeit unsymmetrically, bidentate. Exerting pressure will probably not change its symmetry, and a change in the i.r. pattern is therefore not likely.

In Table 7 the Δ values for the $\nu_1 + \nu_4$ splitting in the i.r. spectra of the compounds ML(NO_3)$_2$ are listed. According to Lever's criteria,[11] the values for the copper and cobalt compounds indicate bidentate nitrate co-ordination. However, the crystal structure of the copper compound (see above) shows one ionic and one unidentate nitrate group. The presence of the ionic nitrate makes the interpretation of the i.r. spectra more difficult, as the second peak was not always observed distinctly. Apparently this peak coincides with the peak due to the ionic nitrate. With Lever's method it is also not possible to recognize nitrate groups which co-ordinate in a anisobidentate mode. It is clear that the mode of co-ordination of nitrate ions cannot be established from i.r. spectral data alone.

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