Crystal and Molecular Structures of Dinitritobis(pyridine)zinc(II), Bis(2-methylpyridine)dinitritozinc(II), and Dinitritobis(quinoline)-nickel(II) *

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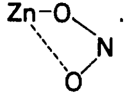
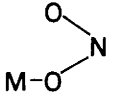
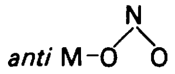
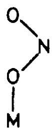
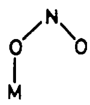
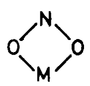
The crystal and molecular structures of the title complexes are reported. The overall geometry of the three complexes is similar, with the amine ligands in each case occupying *cis* co-ordination sites. However, the ways in which the nitrite groups are bound to the metal ions differ considerably, these chelating approximately symmetrically in the nickel compound, but with a marked asymmetry in the compound [Zn(pyridine)$_2$(NO$_2$)$_2$]. In [Zn(2-methylpyridine)$_2$(NO$_2$)$_2$] the nitrite groups are best thought of as unidentate nitrito-ligands with the second oxygen atom semico-ordinated to the metal: . The variation in the manner of nitrite co-ordination is probably influenced both by the electronic structure of the metal ions and the steric requirements of the amine ligands. The relationship between the i.r. frequencies and the co-ordination geometry of oxygen-bound nitrite groups is discussed, and it is shown that it is impossible to distinguish between *syn*  and *anti*  nitrito-groups unambiguously using this technique.

The nitrite ion is an unusual ligand because of the large number of different ways in which it can bond to a metal ion, nine distinct co-ordination types having so far been identified unambiguously in metal complexes.† Considerable interest has been shown in the factors which influence nitrite stereochemistry and it has been suggested that both electronic and steric effects may be important in this respect.[1] Much attention has also been paid to the identification of the various methods of bonding from the i.r.[2] and electronic spectra ‡ of nitrite complexes.

Unidentate nitrito-co-ordination may occur by either an *anti* or *syn* arrangement [(I) and (II) below]. It is apparent that


(I)


(II)


(III)

anti co-ordination should minimize ligand–ligand repulsions in a complex, while the *syn* arrangement could well allow a significant bonding interaction between the second nitrite oxygen atom and the metal. The latter type of structure can also be considered to be a highly asymmetric form of chelation (III). All three forms of bonding are known in different zinc(II) compounds.[3,4] The ease of their interconversion in any particular molecule may well have important implications on the interpretation of the kinetic behaviour of cobalt(III) nitrite complexes, since it has recently been shown [5] that in the thermodynamically unstable nitrito-isomers of this metal ion, which are known to contain *anti* nitrito-groups in the solid state,[6] the two nitrite oxygen atoms interchange at a rate comparable to that of the nitrito–nitro reaction. It seems feasible that this 'scrambling' of the nitrite oxygen atoms occurs *via* a reaction pathway involving a *syn* nitrito-group which then undergoes a pseudo-rotation to interchange the oxygen atoms bound to the metal *via* a symmetrically chelated intermediate.

One of the most widely used methods of investigating the nitrite bonding in a complex is i.r. spectroscopy and it has been suggested [7,8] that the energy difference between the two nitrite NO stretching frequencies is especially useful as a diagnostic test of nitrite co-ordination type. In a previous publication [9] the i.r. spectra of a number of complexes of general formula [Zn(L)$_2$(NO$_2$)$_2$] were reported, where L is a heterocyclic amine. These were interpreted [7,9] as suggesting that when L is pyridine, isoquinoline, and 3- and 4-methylpyridine the nitrite ions are present as asymmetrically chelated groups, while in the 2-methylpyridine complex unidentate nitrito-groups occur. This contrasts with the analogous quinoline- and 2-methylpyridine–nickel(II) complexes, where the electronic and i.r. spectra suggest [10] that symmetrically chelated nitrite groups are present.

The electronic spectra of the latter complexes are of interest, as several compounds of the form [NiL(NO$_2$)$_2$] (L = a diamine) containing chelating nitrite ions have been observed [11,12] to exhibit an anomalous band at *ca.* 23 000 cm^{-1} which has been assigned as a spin-forbidden internal nitrite

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* *Supplementary data available* (No. SUP 23656, 30 pp.): structure factors, thermal parameters, ligand H and non-H geometries, ligand least-squares planes. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

† Examples of eight of these are given in ref. 1; a further type of tridentate co-ordination has recently been reported in the complex [Ni(H$_2$NCH$_2$CH$_2$NH$_2$)$_2$(NO$_2$)]$_2$[BPh$_4$]$_2$: A. Gleizes, A. Meyer, M. A. Hitchman, and O. Kahn, *Inorg. Chem.*, 1982, **21**, 2257.

‡ For a summary of the electronic spectra of nitrite complexes see ref. 1, p. 84.

Table 1. Specific crystallographic details

Compound	(1)	(2)	(3)
Formula	$C_{10}H_{10}N_4O_4Zn$	$C_{12}H_{14}N_4O_4Zn$	$C_{18}H_{14}N_4NiO_4$
M	315.6	343.6	409.1
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}(C_i^1$, no. 2)	$C2/c(C_{2h}^6$, no. 15)	$Pcab(D_{2h}^{15}$, no. 61)
a/Å	12.193(5)	14.184(2)	28.08(2)
b/Å	7.953(4)	7.853(1)	17.072(9)
c/Å	7.573(3)	15.000(2)	7.465(9)
α/°	67.08(3)		
β/°	87.41(3)	112.14(1)	
γ/°	88.18(4)		
U/Å^3	675.6(5)	1 547.4(4)	3 578(3)
D_c/g cm^{-3}	1.55	1.48	1.52
Z	2	4	8
F(000)	320	704	1 680
$2\theta_{max}$/°	45	50	45
N	1 777	1 371	2 334
N_o	1 499	1 157	1 113
R	0.033	0.027	0.040
R'	0.041	0.035	0.044
μ_{Mo}/cm^{-1}	18.0	15.8	11.0
Specimen size/mm	0.30 × 0.25 × 0.10	0.14 × 0.25 × 0.45	0.14 × 0.04 × 0.25

Table 2. Atom co-ordinates for complex (1)

	Ligand A			Ligand B		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Zn	0.252 96(3)	0.126 96(6)	0.098 71(6)			
Nitrite						
O	0.215 0(3)	0.315 9(5)	−0.170 5(4)	0.295 0(3)	−0.147 5(4)	0.239 2(5)
N	0.285 0(4)	0.282 7(6)	−0.279 7(5)	0.226 6(4)	−0.223 4(6)	0.177 5(8)
O′	0.350 5(3)	0.161 7(5)	−0.189 8(6)	0.161 8(3)	−0.113 4(6)	0.072 1(7)
Pyridine						
N(1)	0.382 6(2)	0.227 7(4)	0.191 3(4)	0.119 1(2)	0.193 8(4)	0.237 4(4)
C(2)	0.378 1(4)	0.387 5(6)	0.211 4(6)	0.023 8(3)	0.238 9(6)	0.149 5(7)
H(2)	0.306(3)	0.451(5)	0.188(5)	0.025(3)	0.240(5)	0.028(5)
C(3)	0.463 6(4)	0.454 6(6)	0.271 2(6)	−0.067 0(4)	0.293 5(7)	0.225 9(8)
H(3)	0.455(4)	0.570(6)	0.279(6)	−0.134(4)	0.326(6)	0.159(6)
C(4)	0.560 0(4)	0.354 2(7)	0.311 3(7)	−0.061 8(4)	0.302 5(7)	0.400 1(8)
H(4)	0.615(4)	0.397(6)	0.343(6)	−0.122(4)	0.334(6)	0.448(6)
C(5)	0.567 0(4)	0.194 6(7)	0.285 1(7)	0.034 0(4)	0.252 4(8)	0.495 0(8)
H(5)	0.631(4)	0.115(6)	0.318(6)	0.037(4)	0.253(7)	0.614(8)
C(6)	0.476 7(3)	0.133 7(6)	0.228 0(6)	0.122 8(4)	0.200 6(6)	0.409 8(6)
H(6)	0.480(3)	0.027(6)	0.201(6)	0.197(4)	0.173(5)	0.472(6)

transition. It was proposed[11] that the unusually high intensity of this peak may be associated with the non-centrosymmetric nature of the complexes. It is therefore important to learn whether the amine ligands in compounds of the type $[Ni(L)_2(NO_2)_2]$ (L = an amine) occupy *cis* or *trans* co-ordination sites, since if the latter situation occurred, a centrosymmetric molecule could well result.

In order to investigate these points, and to clarify the influence which the amine substituents and the nature of the metal ion have on nitrite co-ordination geometry, the crystal and molecular structures of the compounds $[Zn(py)_2(NO_2)_2]$ (1), $[Zn(2Me\text{-}py)_2(NO_2)_2]$ (2), and $[Ni(quin)_2(NO_2)_2]$ (3) have been determined (py = pyridine, 2Me-py = 2-methylpyridine, and quin = quinoline). The results are presented in the present paper, together with a discussion on the way in which the nitrite i.r. stretching frequencies are related to co-ordination geometry for oxygen-bonded nitrite groups.

Results and Discussion

Specific crystallographic details for the compounds $[Zn(py)_2(NO_2)_2]$ (1), $[Zn(2Me\text{-}py)_2(NO_2)_2]$ (2), and $[Ni(quin)_2(NO_2)_2]$ (3) are given in Table 1, with atomic co-ordinates being listed in Tables 2, 3, and 4 respectively. Each consists of monomeric molecular units and the molecular structure of each complex, viewed down the bisector of the angle formed by the amine nitrogen atoms with the metal, is shown in Figure 1(*a*)—(*c*), respectively. The co-ordination geometry about each metal is given in Table 5, and the bond distances and angles of the nitrito-ligands are shown in Table 6.

The overall geometry of the three molecules is clearly very similar. In the case of $[Ni(quin)_2(NO_2)_2]$, the ligand donor atoms form a distorted octahedral arrangement about the metal, with the amine nitrogen atoms occupying neighbouring co-ordination sites. It is perhaps surprising that the ligands adopt a *cis* rather than a *trans* configuration, since it might be

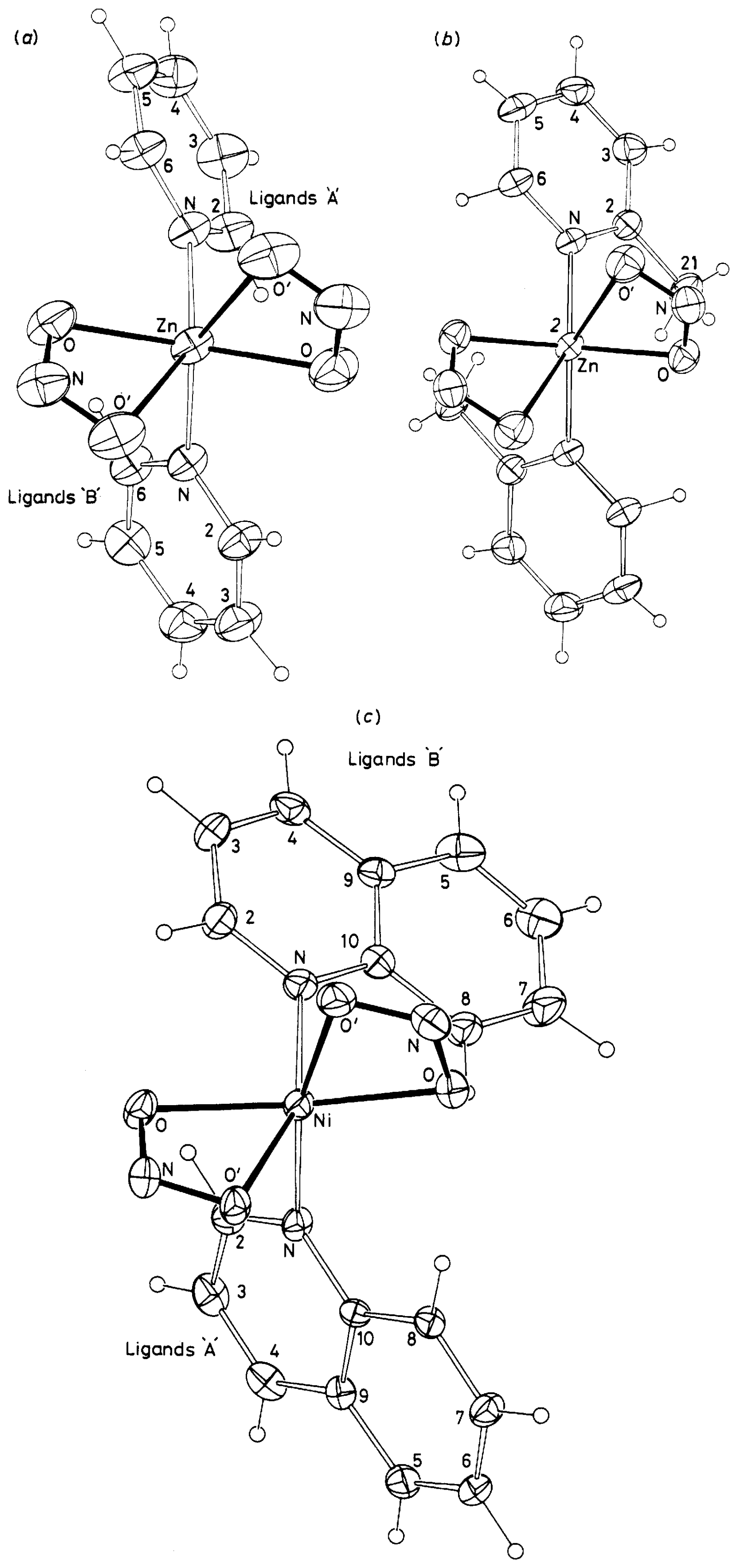

Figure 1. Molecular projections of (*a*) $[Zn(py)_2(NO_2)]$ (1), (*b*) $[Zn(2Me\text{-}py)_2(NO_2)_2]$ (2), and (*c*) $[Ni(quin)_2(NO_2)_2]$ (3), viewed in each case approximately down the bisector of the angle made by the amine ligand atoms with the metal. Hydrogen atoms have an arbitrary radius of 0.1 Å. 20% Thermal ellipsoids are shown for the non-hydrogen atoms

thought that the latter disposition would minimize steric interference between the bulky amine ligands. (It has been suggested[13] that steric hindrance significantly affects the nature of the complexes formed by α-substituted amines.) The non-bonding contacts less than 2.7 Å for this complex are shown in Table 7, from which it may be seen that several interactions at or about the van der Waals limit[14] occur. The ligand co-ordination geometry in [Ni(quin)$_2$(NO$_2$)$_2$] is in fact very similar to that observed[7] in [Ni(tetmen)(NO$_2$)$_2$] (tetmen = *NNN'N'*-tetramethylethylenediamine), except for the fact that the angle subtended by the amine nitrogen atoms at the metal is 97° in the former compound, but 86° in the latter,[7] this second value presumably being influenced by the constraints imposed by the chelate ring. The single-crystal electronic spectra of [Ni(tetmen)(NO$_2$)$_2$] and other nickel(II) complexes containing chelating nitrite ions have been the subject of some interest,[11,12] in particular because of the presence of an anomalous band centred at *ca.* 23 000 cm^{-1} which exhibits considerable vibrational fine structure at low temperature. It was suggested[11] that the unusually high intensity of the band might be associated with the non-centrosymmetric nature of the complexes which have so far been studied. This hypothesis could be tested by measuring the electronic spectrum of a centrosymmetric compound of the form *trans*-[Ni(L)$_2$(NO$_2$)$_2$] containing chelating nitrite groups. The electronic spectrum of [Ni(quin)$_2$(NO$_2$)$_2$] is broadly similar to that of the [Ni(tetmen)(NO$_2$)$_2$] complex,[10] but now that it is known that both molecules have a *cis* geometry, the question of the relationship between the electronic spectra and stereochemistry of complexes of this type remains unresolved.

While the overall shapes of the two zinc complexes are quite similar to that of the nickel compound (Figure 1), there are significant differences in the arrangement of the ligand donor atoms (Table 5). The basic molecular shape of the complexes is shown schematically in Figure 2, and some im-

Table 3. Atom co-ordinates for complex (2)

Atom	*x*	*y*	*z*
Zn	0	0.394 87(5)	$\frac{1}{4}$
Nitrite			
O	0.124 3(1)	0.498 4(3)	0.236 2(1)
N	0.154 3(2)	0.619 9(3)	0.295 9(2)
O′	0.103 7(2)	0.636 4(3)	0.346 0(2)
2-Methylpyridine			
N(1)	0.053 4(2)	0.247 7(2)	0.373 6(1)
C(2)	0.125 1(2)	0.128 0(3)	0.391 8(2)
C(21)	0.159 0(3)	0.078 4(5)	0.312 4(3)
H(21A)	0.109(4)	0.032(6)	0.262(4)
H(21B)	0.170(3)	0.170(5)	0.279(3)
H(21C)	0.211(3)	−0.003(5)	0.337(2)
C(3)	0.166 2(2)	0.052 3(4)	0.482 0(2)
H(3)	0.213(2)	−0.030(4)	0.487(2)
C(4)	0.133 8(3)	0.100 2(5)	0.553 0(2)
H(4)	0.160(3)	0.039(5)	0.611(3)
C(5)	0.059 3(3)	0.220 8(5)	0.533 7(2)
H(5)	0.033(3)	0.261(5)	0.572(3)
C(6)	0.020 4(2)	0.291 8(4)	0.444 6(2)
H(6)	−0.036(2)	0.370(4)	0.429(2)

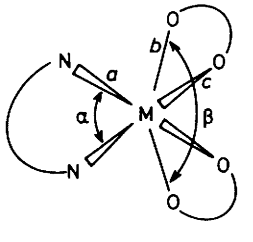

Figure 2. Idealized ligand co-ordination geometry of the complexes; the values of the indicated parameters are given in Table 8

Table 4. Atom co-ordinates for complex (3)

		Ligand A			Ligand B	
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Ni	0.142 37(3)	0.109 73(5)	0.080 78(13)			
Nitrite						
O	0.097 7(2)	0.166 7(3)	0.265 2(7)	0.196 9(2)	0.032 9(3)	0.018 9(7)
N	0.094 0(2)	0.108 8(4)	0.367 1(8)	0.226 9(2)	0.063 8(4)	0.1258 (9)
O′	0.116 9(2)	0.050 6(3)	0.314 2(7)	0.209 5(2)	0.120 6(3)	0.207 8(6)
Quinoline						
N(1)	0.090 0(2)	0.057 7(3)	−0.072 4(8)	0.163 5(2)	0.192 3(3)	−0.106 2(8)
C(2)	0.096 2(3)	−0.018 3(4)	−0.109 3(11)	0.171 6(3)	0.166 0(4)	−0.268 3(11)
H(2)	0.124(−)	−0.045(−)	−0.067(−)	0.164(−)	0.111(−)	−0.295(−)
C(3)	0.062 2(3)	−0.063 5(5)	−0.203 2(13)	0.190 4(3)	0.212 5(5)	−0.408 0(11)
H(3)	0.066(−)	−0.118(−)	−0.229(−)	0.196(−)	0.189(−)	−0.525(−)
C(4)	0.021 3(3)	−0.030 2(4)	−0.256 4(12)	0.200 1(3)	0.288 5(5)	−0.376 9(10)
H(4)	−0.003(−)	−0.061(−)	−0.324(−)	0.211(−)	0.322(−)	−0.476(−)
C(5)	−0.029 7(3)	0.087 5(5)	−0.275 4(12)	0.201 1(3)	0.399 0(4)	−0.162 2(10)
H(5)	−0.054(−)	0.058(−)	−0.341(−)	0.213(−)	0.435(−)	−0.256(−)
C(6)	−0.035 0(3)	0.163 7(5)	−0.243 5(13)	0.192 3(3)	0.427 4(4)	0.005 0(12)
H(6)	−0.064(−)	0.189(−)	−0.289(−)	0.200(−)	0.482(−)	0.034(−)
C(7)	−0.000 9(3)	0.207 4(4)	−0.154 0(13)	0.174 5(3)	0.376 7(4)	0.136 1(10)
H(7)	−0.008(−)	0.262(−)	−0.126(−)	0.167(−)	0.398(−)	0.257(−)
C(8)	0.040 7(3)	0.172 7(4)	−0.102 2(12)	0.164 9(3)	0.299 8(4)	0.104 4(10)
H(8)	0.065(−)	0.204(−)	−0.042(−)	0.150(−)	0.265(−)	0.199(−)
C(9)	0.012 6(3)	0.049 2(4)	−0.223 8(11)	0.191 9(2)	0.319 3(4)	−0.204 3(9)
C(10)	0.048 5(3)	0.091 9(4)	−0.133 4(9)	0.173 7(2)	0.270 2(4)	−0.069 0(10)

Table 5. Metal co-ordination environment. The entries in column *r* are the metal–ligand distances (Å). Other entries are the angles subtended at the metal atom by the two relevant atoms at the head of the row and column. For compound (2) italicized atoms are generated by the intramolecular two-fold rotor

(*a*) Compound (1)

	r_{Zn-L}	O(A)	O(A′)	N(1B)	O(B)	O(B′)
N(1A)	2.062(3)	107.5(1)	91.3(1)	102.7(1)	96.2(1)	151.1(1)
O(A)	2.070(3)		54.9(1)	94.7(1)	140.9(2)	95.6(2)
O(A′)	2.362(4)			149.4(1)	94.9(1)	87.8(2)
N(1B)	2.068(3)				110.2(1)	92.3(1)
O(B)	2.081(3)					55.2(1)
O(B′)	2.320(3)					

(*b*) Compound (2)

	r_{Zn-L}	O	O′	*N(1)*	*O*	*O′*
N(1)	2.071(2)	106.12(8)	88.30(8)	112.18(8)	99.85(9)	151.29(11)
O	2.021(2)		53.63(10)	99.85(9)	132.58(9)	88.98(9)
O′	2.497(2)			151.29(9)	88.98(9)	81.17(8)
N(1)					106.12(8)	88.30(8)
O						53.63(10)

(*c*) Compound (3)

	r_{Ni-L}	O(A)	O(A′)	N(1B)	O(B)	O(B′)
N(1A)	2.065(6)	97.9(2)	90.5(2)	97.1(2)	97.5(2)	156.9(2)
O(A)	2.101(5)		59.0(2)	107.3(2)	151.9(2)	101.4(2)
O(A′)	2.138(5)			165.3(2)	97.5(2)	88.5(2)
N(1B)	2.071(6)				94.0(2)	89.3(2)
O(B)	2.068(5)					59.8(2)
O(B′)	2.118(5)					

Table 6. Nitrite geometry; distances (Å) and angles (°)

	Compound (1)			Compound (3)	
	Nitrite A	Nitrite B	Compound (2)	Nitrite A	Nitrite B
NO	1.255(6)	1.250(7)	1.267(4)	1.251(8)	1.275(8)
NO′	1.231(6)	1.223(6)	1.227(5)	1.249(8)	1.246(8)
MON	103.4(2)	101.9(3)	107.7(2)	94.8(4)	94.9(4)
MO′N	89.7(3)	90.9(4)	85.4(2)	93.1(4)	93.4(4)
ONO′	111.9(5)	111.9(4)	113.2(3)	113.2(6)	111.8(5)

Table 7. Intramolecular non-bonded contacts (Å). Atoms related by the two-fold rotor in (2) are italicized

(*a*) Compound (1)

H(6A) ··· O(B)	2.63(4)
H(2B) ··· O(A)	2.66(4)

(*b*) Compound (2)

H(21B) ··· O	2.68(4)
H(6) ··· *O*	2.52(3)

(*c*) Compound (3)

H(8A) ··· O(A)	2.55(−)
H(8B) ··· O(A)	2.29(−)
H(2A) ··· O(B)	2.52(−)

Table 8. Comparison of some parameters describing the ligand stereochemistry of the complex (see Figure 3 for a definition of the parameters)

	Bond lengths/Å			Angles/°	
Complex	*a*	*b*	*c*	α	β
$[Zn(py)_2(NO_2)_2]$	2.07	2.08	2.34 *	103	141
$[Zn(2Me\text{-}py)_2(NO_2)_2]$	2.07	2.02	2.50	112	133
$[Ni(quin)_2(NO_2)_2]$	2.07	2.09 *	2.13 *	97	152

* Average value.

portant bond distances and angles are compared in Table 8. The most striking difference between the zinc and nickel compounds is in the nitrite co-ordination. In $[Ni(quin)_2(NO_2)_2]$, the metal-oxygen bond distances to each nitrite are quite similar, the *trans*-Ni–O bonds being marginally shorter than the *cis*.[*,15] In the two zinc compounds, however, the co-ordination to each nitrite is markedly asymmetric, with the *trans*-bonded oxygen atoms being much closer to the metal. A chelated nitrite [(III) above] may be transformed into a *syn* unidentate group [(II) above] by a rotation about an axis orthogonal to the plane containing the nitrite ion and the metal. In principle a co-ordination geometry lying anywhere between these extremes is possible, and it has been suggested[16] that an important variable in this respect is the ratio of the longer to the shorter M–O bond, *R*(MO). This is expected to

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[*] It is interesting to note that this discrepancy seems to be a feature of the stereochemistry of compounds of general formula [Ni(chelate)$_2$(chelate′)], since in a variety of compounds of formula $[Ni(diamine)_2(NO_2)]X$ containing chelating nitrite ions the *trans*-Ni–N bonds are consistently slightly shorter than the *cis* ones. For a discussion of this see ref. 15.

vary from 1.0 in a symmetrically chelated group to *ca* 1.4 in a *syn* nitrito-group in which the angle MON is *ca.* 120°. In $[Zn(py)_2(NO_2)_2]$ *R*(MO) is 1.13, while in $[Zn(2Me\text{-}py)_2(NO_2)_2]$ it is 1.24, so that on this basis the nitrite in the former compound is best thought of as an asymmetrically chelated group, while that in the latter may be considered as a unidentate nitrito-group, highly distorted so as to allow the second oxygen atom to ' semi-co-ordinate ' to the metal. The distortion away from the essentially symmetrically chelated groups in $[Ni(quin)_2(NO_2)_2]$, where *R*(MO) = 1.02, is such that the lengthening of one Zn–O bond is accompanied by a concomitant shortening of the other (Table 8). The bond lengths to the amine nitrogen atoms remain constant for all three complexes, but the angle NMN increases from 97, to 103, to 112° on going from $[Ni(quin)_2(NO_2)_2]$ to $[Zn(py)_2(NO_2)_2]$ to $[Zn(2Me\text{-}py)_2(NO_2)_2]$ (Figure 2, Table 8). Along the same series the angle OMO produced by the *trans*-co-ordinated oxygen atoms decreases from 152 to 141 to 133°. A regular octahedral geometry implies 90° for the former angle, and 180° for the latter, while a tetrahedral stereochemistry requires both angles to be 109.5°. It therefore seems that the ligand environment in the nickel complex is significantly closer to an octahedral than a tetrahedral arrangement, while the reverse is true for $[Zn(2Me\text{-}py)_2(NO_2)_2]$, with $[Zn(py)_2(NO_2)_2]$ lying approximately midway between the two extremes. Interligand repulsion is expected to decrease on going from a six-co-ordinate towards a four-co-ordinate geometry, and the stereochemical differences between the zinc compounds may be caused by the steric requirements of the substituent in the 2Me-py complex. The presence of several contacts at about the van der Waals limit (Table 7) supports this hypothesis. One would expect steric crowding to be greater in $[Ni(quin)_2(NO_2)_2]$ than in $[Zn(py)_2(NO_2)_2]$, and this is supported by the non-bonding contacts (Table 7). It therefore seems likely that the electronic structure of the metal ion influences the geometry of the nickel(II) complex, tending to favour an octahedral stereochemistry, as has been observed in other compounds of this kind.[7,17] It appears that the barrier to interconversion between chelated and *syn* unidentate nitrite groups may be relatively small, so that this could provide a reaction pathway by which the oxygen atoms of the nitrite groups in complexes such as $[Co(NH_3)_4(ONO)]Cl_2$ become interchanged.[5]

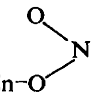
The internal nitrite geometry is of interest and this is given in Table 6. As expected, in each complex the NO bond lengths to the oxygen atoms closer to the metal are shorter than that in $NaNO_2$,[18] while those to the more distant oxygens are longer. However, the effect is not as pronounced as that observed in complexes involving truly unidentate nitrito-groups [average N–O distances for several complexes of divalent metal ions are 1.285(19) Å and 1.177(37) Å [19]]. Moreover, the discrepancy increases progressively along the series $[Ni(quin)_2(NO_2)_2]$ < $[Zn(py)_2(NO_2)_2]$ < $[Zn(2Me\text{-}py)_2(NO_2)_2]$ as the degree of asymmetry of the nitrito-co-ordination increases. The angle ONO has been observed to decrease by *ca.* 2° from the free ion value of 114.9(5)° when the nitrite chelates,[19] and that trend also occurs in the present complexes (Table 6).

Correlation of Nitrite Vibrational Frequencies with Molecular Structures.—It is well known that the nitrite i.r. frequencies can be a useful guide to the nature of its co-ordination.[2] Of the three fundamental modes, the scissoring vibration $\delta(NO_2)$ which occurs at 830 cm^{-1} in $NaNO_2$[20] is the least sensitive to the co-ordination type, although a general trend for this to be raised by 20—30 cm^{-1} from the free-ion value upon chelation has been noted.[10] This vibration occurs at 839, 850, and 867 cm^{-1} in $[Zn(2Me\text{-}py)_2(NO_2)_2]$, $[Zn(py)_2(NO_2)_2]$, and $[Ni(quin)_2(NO_2)_2]$, respectively,[9,10] with the increasing shift from the free-ion value being in line with the trend from unidentate to symmetrical bidentate nitrite co-ordination discussed above.

Table 9. Infrared stretching frequencies and metal–oxygen bond distances in some nitrite complexes

Compound	M–O/ Å	ν(NO)/ cm^{-1}	δ_ν/ cm^{-1}	Ref.
$NaNO_2$		1 261, 1 328	67	20
$[Zn(H_2NCH_2CH_2NH_2)_2(NO_2)]ClO_4$	2.25, 2.27	1 207, 1 277	70	7
$[Ni(tetmen)(NO_2)_2]$	2.07, 2.12	1 200, 1 289	89	7, 10
$[Ni(quin)_2(NO_2)_2]$	2.09, 2.13	1 198, 1 295	97	*a*, 10
$[Zn(tetmen)(NO_2)_2]$	2.07, 2.30	1 183, 1 316	133	7
$[Zn(py)_2(NO_2)_2]$	2.08, 2.34	1 171, 1 351	180	*a*, 9
$[Cu(tetmen)(NO_2)_2]$	2.02, 2.44	1 160, 1 360	200	*b*
$Cs_2[Zn(NO_2)_4]$	2.09, 2.54	1 167, 1 381	214	4, *c*
$[Zn(dmen)_2(ONO)_2]$	2.22, *d*	1 145, 1 380	235	3, 9
$[Zn(2Me\text{-}py)_2(NO_2)_2]$	2.02, 2.50	1 131, 1 370	239	*a* 9
$[Ni(dmen)_2(ONO)_2]$	2.11, *d*	1 130, 1 387	257	*e*
$[Co(NH_3)_5(ONO)]Cl_2$	1.93, *d*	1 065, 1 468	403	6, *f*

[a] Present work. [b] E. E. Luukkonen, *Suom. Kemistil. B*, 1973, **46**, 302. [c] D. M. L. Goodgame and M. A. Hitchman, *J. Chem. Soc. A*, 1967, 612. [d] *anti* Unidentate nitrito-group. [e] A. J. Finney, M. A. Hitchman, C. L. Raston, G. L. Rowbottom, and A. H. White, *Aust. J. Chem.*, 1981, **34**, 2047; D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 1964, 3, 1389. [f] K. Nakamoto, J. Fujita, and H. Murata, *J. Am. Chem. Soc.*, 1958, **80**, 4817.

The behaviour of the two NO stretching frequencies ν_{sym} and ν_{asym} generally provides the best indication of the manner of nitrite co-ordination in a complex; these are given for the present compounds in Table 9. In particular, the energy separation between these has been found to depend upon the degree of asymmetry of the co-ordination to the nitrite oxygen atoms.[1,7] In a symmetrically chelated nitrite group, the difference between ν_{sym} and ν_{asym} is similar to that in the free ion (*ca.* 70 cm^{-1}), while for unidentate nitrito-groups with the *anti* configuration, the separation is *ca.* 245 cm^{-1} (Table 9). For asymmetrically chelated groups, the splitting is observed to lie between these two extremes. On this basis, it was suggested that the nitrite groups in $[Ni(quin)_2(NO_2)_2]$ chelate approximately symmetrically,[10] while those in $[Zn(py)_2(NO_2)_2]$ chelate with a marked asymmetry,[9] and that the complex $[Zn(2Me\text{-}py)_2(NO_2)_2]$ probably contains *anti* unidentate nitrito-groups.[7] The present structural studies have confirmed the first two predictions, but have shown that the latter complex contains *syn* unidentate nitrito-ions, with the formally non-bonded oxygen atom semi-co-ordinated to the metal. The difference between ν_{sym} and ν_{asym} for the  $\mathrm{Zn{-}O}$ groups in $[Zn(2Me\text{-}py)_2(NO_2)_2]$ is in fact virtually identical to that observed for the  $\mathrm{Zn{-}O\ \ O}$ groups in $[Zn(dmen)_2(NO_2)_2]$ (dmen = *NN*-dimethylethylenediamine) (Table 9). The ZnO distance in the latter complex (2.22 Å) is significantly longer than the shorter of the two contacts in the 2Me-py complex

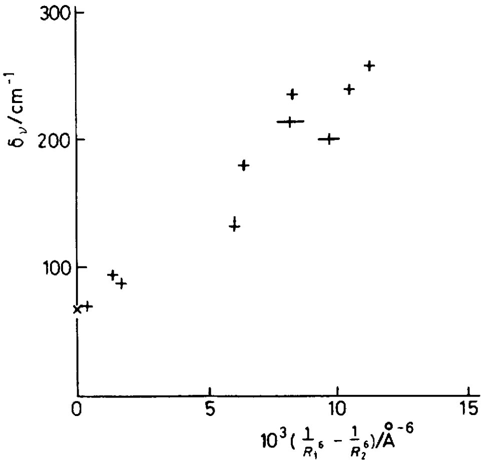


Figure 3. Plot of the difference in nitrite stretching frequencies, δ_V, against the difference between the inverse of the sixth power of the metal–oxygen bond distances for all transition-metal complexes containing chelated and unidentate nitrito-groups for which both structural and i.r. data are available. The data are from Table 9, and the value for $NaNO_2$ is shown by a cross (×)

(2.02 and 2.50 Å) and it would seem that the combined effect on the nitrite of the two interactions in $[Zn(2Me\text{-}py)_2(NO_2)_2]$ is about the same as that of the single interaction in $[Zn(dmen)_2(NO_2)_2]$. The perturbation produced by a ligand on the metal in a complex is often taken to be inversely proportional to some power of the bond distance.[21] On this basis the reverse might also be true, with the inequivalence in the two nitrite NO bond strengths, as measured by the difference in the stretching frequencies, δ_v, being related to the metal–oxygen bond distances R_1 and R_2 by an expression of the form shown below. For chelated, asymmetrically chelated, and

$$\delta_V \propto \left[\frac{1}{R_1^n} - \frac{1}{R_2^n}\right]$$

unidentate nitrito-groups bound to the first-row transition metal ions (including zinc) this relationship is obeyed quite well if *n* is *ca.* 6, even when the data available for Co^{III} nitrito-complexes are included, as can be seen from Figure 3. It therefore seems that although i.r. spectroscopy cannot distinguish unambiguously between *syn* and *anti* nitrito-coordination, it can give a good indication of the relative perturbation felt by the two nitrite oxygen atoms in a complex.

Experimental

Preparation of Complexes.—Crystals of the zinc(II) and nickel(II) complexes were prepared by the methods described in the literature, the nature of the complexes being confirmed by a comparison of the i.r. spectra with those previously reported.

Structure Determinations.—Details specific to each compound are given in Table 1. Specimens were mounted in capillaries. Unique data sets were measured for each compound within a $2\theta_{max.}$ limit determined by the extent of the data, using a four-circle diffractometer in conventional $2\theta/\theta$ scan mode, and equipped with a monochromatic Mo-K_α radiation source ($\lambda = 0.7106_9$ Å). *N* Independent reflections were obtained in each case, and of these N_o with $I > 3\sigma(I)$ were considered 'observed' and used in the least-squares refinement after correction for absorption. For the non-hydrogen atoms, anisotropic thermal parameters were refined. In the more precise Zn structures x,y,z,U_H(isotropic) were refined; in the Ni structure where this was not possible, they were included as constrained estimates. For the smaller Zn structures full-matrix least-squares refinement was used; for the larger Ni structure, 9 × 9 block diagonal. At convergence parameter shifts were less than 0.2σ, residuals R,R' being quoted, with reflection weights being $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. Neutral-atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f', f'').[22] Computation used the *X*-RAY 76 program system implemented on a Perkin-Elmer 3240 computer.[23] Atom numbering for the non-hydrogen atoms in each case is shown in the Figures; hydrogen-atom numbering follows that of the parent C or N atom, suffixed A or B where distinction is necessary.

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