Crystal and Molecular Structure of 1,3-Bis(2-iminobenzylideneimino)-propanenickel(II)

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Crystals of the title compound are orthorhombic with $a = 7{\cdot}69$, $b = 24{\cdot}42$, and $c = 7{\cdot}94$ Å, space group *Pnma* (D_{2h}^{16}, no. 62). A three-dimensional *X*-ray analysis of the structure was made with Weissenberg photographic data, estimated visually (783 independent reflections). The structure was solved by conventional Patterson and Fourier methods and refined by block-diagonal least-squares to a final *R* of 0·069. The [NiN_4] co-ordination polyhedron [Ni–N = 1·860(7) and 1·923(7) Å] is essentially planar (Ni atom 0·04 Å out of the symmetry imposed N_4 plane), but the molecule has an oblique-puckered conformation, with the aromatic moieties of the ligand inclined at 36·6° to one another, and the chelate ring containing the trimethylene moiety has an uncommon symmetrical 'boat' conformation.

As part of a continuing study [1,2] of the structure and reactions of metal compounds of dianionic N_4 ligands, we report here on the crystal and molecular structure of the compound [Ni(abtn)] (I).

Structural parameters on such a system, containing a trimethylene chelate ring, were deemed useful because: (a) very few structures have been determined of compounds containing such a chelate ring; and (b) crystalline [Co(abtn)], which is isomorphous with the nickel compound, has a band at $9{\cdot}7\ 10^3\ cm^{-1}$ in its electronic spectrum which moves to *ca.* $11{\cdot}3\ 10^3\ cm^{-1}$ when the compound is dissolved in solvents which do not co-ordinate to the metal.[3,4] This latter appears to be what one

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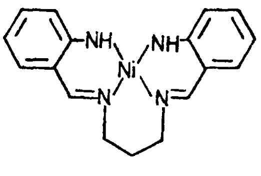
[1] B. M. Higson and E. D. McKenzie, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 209; *J.C.S. Dalton*, 1972, 269.

[2] N. A. Bailey, T. A. James, J. A. McCleverty, E. D. McKenzie, R. D. Moore, and J. M. Worthington, *J.C.S. Chem. Comm.*, 1972, 681.

[3] E. D. McKenzie and J. M. Worthington, unpublished data.

[4] M. Green and P. A. Tasker, *J. Chem. Soc.* (*A*), 1970, 3105.

would normally classify as a '*d*–*d*' transition, so the origin of the variation in position is of some interest.



(I)

Both the Co and Ni compounds have virtually identical *X*-ray powder diffraction paterns, and the Ni was chosen for the analysis (with Cu-K_α radiation).

EXPERIMENTAL

Opaque crystals with a green reflection were obtained by slow evaporation from *NN*′-dimethylformamide. The crystal (0·28 × 0·14 × 0·07 mm) was mounted in a thin-walled glass capillary. Unit-cell dimensions were measured from precession photographs obtained with Zr-filtered Mo-K_α radiation. Agreement between observed and calculated powder diffraction patterns proved that the crystal used was representative of the bulk sample.

Crystal Data.—$C_{17}H_{18}N_4Ni$, M = 337·1, Orthorhombic, a = 7·69(2), b = 24·42(6), c = 7·94(2) Å, V = 1491 Å^3. D_m = 1·50 g cm^{-3} (by flotation), D_c = 1·501 g cm^{-3}, Z = 4, F(000) = 704. Cu-K_α radiation, λ = 1·5418 Å; μ(Cu-K_α) = 18·0 cm^{-1}. Space group *Pnma* (D_{2h}^{16}, no. 62) or *Pn*2$_1$*a* (a non-standard setting of C_{2v}^{9}, no. 33) from the systematic absences; the former was proved by the analysis.

Layers {0—6*kl*} were collected photographically by the equi-inclination Weissenberg method using Ni-filtered Cu-K_α radiation, and intensities were estimated visually. The usual Lorentz, polarization, and spot-shape corrections were applied; and precession *h*0*l* and *hk*0 photographic data (Mo-K_α) measured for the *initial* layer scaling. No corrections were made for absorption. A total of 783 independent reflections, derived only from the Cu-K_α data, were used in the final refinement.

A Patterson synthesis showed the Ni atom very close to (0,¼,0) and a Fourier synthesis based on this atom had pseudo-*mmm* symmetry about this position. Only in the first co-ordination sphere of the nickel was the resolution good enough for the determination of atomic co-ordinates of other atoms. Even so, there was a choice of eight possible positions for the nitrogen atoms. Disregarding chemically absurd possibilities, two models were chosen: an expected coplanar one, and a flattened tetrahedral one.

Structure factors phased on both models in space group *Pn*2$_1$*a* were used for further Fourier syntheses; but only in the case of the four coplanar model did these give the positions of the other non-hydrogen atoms. So the alternative (tetrahedral) model was discarded.

The four coplanar model indicated mirror symmetry in the molecule, and block-diagonal least-squares refinement of the atomic co-ordinates of all non-hydrogen atoms, using isotropic thermal parameters in space group *Pnma*, reduced *R* to 0·202.

Inter-layer scales were recalculated by scaling to this structure and the precession data were removed from the data set. Further refinement reduced *R* to 0·113. Inclusion, but non-variation, of the calculated positions for the hydrogen atoms (all were clearly detected on a difference Fourier and isotropic *B* factors were assigned as 0·5 Å^2 higher than those of the atoms to which they were attached) reduced *R* to 0·094.

The (1,0,1) reflection appeared to be subject to extinction and was removed from the data set. New, and final, inter-layer scales were calculated, and inclusion of these, and isotropic thermal parameters for the nickel atom reduced *R* to 0·080.

In the final block-diagonal least-squares refinement, the following scheme was used: (i) CH,CH$_2$ and NH were refined as rigid groups of fixed orientation using CH distances of 0·98 Å and NH distances[5] of 0·85 Å. Translational parameters for each group were refined together with anisotropic vibrational parameters for C or N atoms, but isotropic ones for H. The necessary constraints were imposed on the refinement of the CH$_2$ group which lies in a mirror plane.

(ii) The Ni atom, with anisotropic thermal parameters, was constrained to stay within the mirror plane. Anomalous dispersion corrections ($\Delta f'$ and $\Delta f''$)[6] were included for this atom.

(iii) For all other atoms, refinement of positional and anisotropic vibrational parameters was allowed.

When all parameter shifts had dropped below one-sixth of their e.s.d.s, the final *R* was 0·069.

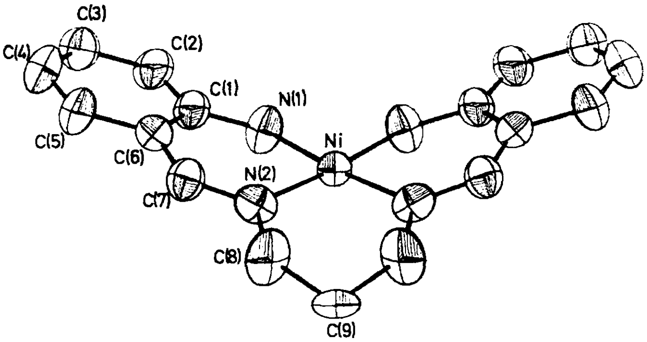
Atomic scattering factors for neutral atoms were taken from International Tables.[6] Observed structure amplitudes and calculated structure factors are tabulated in Supplementary Publication No. SUP 20988 (10 pp., 1 microfiche).*

Programmes used are part of the Sheffield *X*-ray system. Calculations were performed on the Sheffield University ICL 1907 computer.

The final atomic positional and vibrational parameters, with estimated standard deviations, are listed in Table 1.

RESULTS AND DISCUSSION

The molecular geometry is shown in the Figure, together with the atom labelling scheme. Details of the various bond lengths and angles are in Table 2; and relevant equations of least-squares planes and interplanar angles are listed in Table 3.



Molecular geometry and the atom labelling scheme

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* For details of Supplementary Publications see Notice to Authors, No. 7, *J.C.S. Dalton*, 1973, Index issue.

[5] P. Coppens and A. Vos, *Acta Cryst.*, 1971, **B27**, 146; G. J. Kruger and G. Gafner, *ibid.*, p. 326; D. L. Smith and E. K. Barrett, *ibid.*, p. 419.

[6] 'International Tables for *X*-Ray Crystallography,' vol. III Kynoch Press, Birmingham, 1962.

TABLE 1

Atomic positions and thermal vibrational parameters, with estimated standard deviations in parentheses

(a) Atomic positions ($\times 10^4$) of the non-hydrogen atoms

Atom	x/a	y/b	z/c
Ni	66(3)	2500(0)	286(2)
N(1)	−1504(9)	1986(3)	1107(9)
N(2)	1506(9)	1920(3)	−574(8)
C(1)	−1809(12)	1455(3)	678(10)
C(2)	−3276(13)	1177(4)	1271(12)
C(3)	−3572(15)	634(4)	798(14)
C(4)	−2379(14)	367(4)	−292(15)
C(5)	−936(13)	616(3)	−792(13)
C(6)	−599(11)	1177(3)	−333(11)
C(7)	967(12)	1406(3)	−813(11)
C(8)	3284(13)	2003(4)	−1124(14)
C(9)	4184(16)	2500(0)	−446(14)

(b) Hydrogen atomic positions ($\times 10^3$) and isotropic thermal vibrational parameters

H(1) [a]	−215	210	190	4·5
H(2)	−409	137	200	5·5
H(3)	−462	44	119	6·5
H(4)	−259	−1	−63	7·0
H(5)	−12	42	−152	6·0
H(7)	177	116	−141	4·5
H(81)	396	168	−79	6·0
H(82)	328	203	−235	6·0
H(91)	411	250	79	5·0
H(92)	541	250	−79	5·0

(c) Anisotropic thermal vibrational parameters [b] ($\times 10^4$) for the non-hydrogen atoms

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
Ni	127(4)	13(1)	118(2)	0(0)	13(7)	0(0)
N(1)	199(17)	15(1)	168(13)	−3(7)	85(24)	−16(8)
N(2)	129(15)	20(1)	146(13)	−2(7)	38(21)	18(7)
C(1)	174(19)	14(1)	149(15)	2(8)	0(27)	−11(8)
C(2)	205(21)	18(2)	233(20)	8(10)	−31(35)	−30(10)
C(3)	296(28)	18(2)	307(25)	27(12)	−99(42)	−49(12)
C(4)	287(27)	16(2)	374(28)	−19(13)	−61(48)	−11(11)
C(5)	250(25)	15(2)	282(23)	−20(11)	−16(37)	4(10)
C(6)	172(19)	15(1)	171(14)	2(9)	−30(28)	4(8)
C(7)	193(20)	16(2)	172(16)	−7(9)	14(30)	6(9)
C(8)	178(22)	21(2)	331(25)	−19(12)	153(39)	−5(11)
C(9)	138(26)	25(3)	174(24)	0(0)	−62(42)	0(0)

[a] Hydrogen on carbon or nitrogen takes the same number as the heavier atom, with pairs on the same carbon distinguished by a following 1 or 2. Since there are no hydrogens on C(1) or N(2), this causes no ambiguity. [b] The expression for the temperature factors is: $\exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + klb_{23} + hlb_{13} + hkb_{12})]$.

TABLE 2

Interatomic distances and angles with estimated standard deviations in parentheses

(*i*) Bond lengths/Å

N–N(1)	1·860(7)	C(2)–C(3)	1·40(2)
Ni–N(2)	1·923(7)	C(3)–C(4)	1·42(2)
N(1)–C(1)	1·36(1)	C(4)–C(5)	1·33(1)
N(2)–C(7)	1·34(1)	C(5)–C(6)	1·44(1)
N(2)–C(8)	1·45(1)	C(6)–C(7)	1·38(1)
C(1)–C(2)	1·40(1)	C(8)–C(9)	1·50(1)
C(1)–C(6)	1·40(1)		

(*ii*) Bond angles (°)

N(1)–Ni–N(2)	90·1(3)	C(1)–C(2)–C(3)	120·1(9)
N(1)–Ni–N(1′)	84·9(3)	C(2)–C(3)–C(4)	119·7(9)
N(2)–Ni–N(2′)	94·9(3)	C(3)–C(4)–C(5)	120·8(10)
Ni–N(1)–C(1)	131·8(5)	C(4)–C(5)–C(6)	120·8(9)
Ni–N(2)–C(7)	123·3(4)	C(5)–C(6)–C(7)	118·1(6)
Ni–N(2)–C(8)	123·2(4)	C(5)–C(6)–C(1)	119·0(6)
C(7)–N(2)–C(8)	112·4(4)	C(1)–C(6)–C(7)	122·7(6)
N(1)–C(1)–C(2)	121·1(6)	C(6)–C(7)–N(2)	127·7(8)
N(1)–C(1)–C(6)	119·3(6)	N(2)–C(8)–C(9)	116·1(7)
C(2)–C(1)–C(6)	119·6(6)	C(8)–C(9)–C(8′)	108·4(7)

Bond lengths and angles are normal and there are no abnormally short intermolecular contacts.

The nickel(II) atom has an essentially planar co-ordination polyhedron as expected.[1,7] The N_4 plane is symmetry imposed [with a mirror plane perpendicular to the N_4 co-ordination plane bisecting Ni and C(9)] and the metal is only 0·04 Å out of this plane. The two independent Ni–N bond lengths are significantly different at 1·923(7) and 1·860(7) Å, thus reflecting their nature as neutral and anionic ligands respectively. These values compare favourably with those in other four-co-planar nickel(II) compounds.

TABLE 3

Equations to some least-squares planes given in the form $lX + mY + nZ = d$ (where X, Y, and Z are co-ordinates in Å referred to the axes a, b, and c). The deviations (Å) of the various atoms from these planes are given in brackets

		l	m	n	d
Plane (1)	N(1), N(2), N(1′), N(2′) [Ni −0·038, C(8) −0·30, C(7) 0·38, C(1) 0·41]	−0·4994	−0·0000	−0·8664	−0·1838
Plane (2)	N(1), N(2), C(1), C(6), C(7) [Ni −0·39, C(1) 0·01, C(6) −0·03, C(7) 0·03, C(8) 0·18, N(1) 0·00, N(2) −0·01]	0·4539	−0·3100	0·8354	−1·2945
Plane (3)	C(1)—C(6) [C(1) −0·02, C(2) 0·01, C(3) 0·01, C(4) −0·03, C(5) 0·02, C(6) 0·01, C(7) 0·12, N(1) −0·04]	0·4983	−0·3147	0·8079	−1·3557
Plane (4)	N(1), N(2) C(1)—C(7) [Ni −0·40, N(1) −0·04, N(2) 0·01, C(1) −0·02, C(2) 0·04, C(3) 0·04, C(4) −0·03, C(5) −0·02, C(6) −0·03, C(7) 0·05]	0·4745	−0·3138	0·8224	−1·3087
Plane (5)	Ni, N(2), N(2′)	−0·5247	0·0000	−0·8513	−0·2200
Plane (6)	N(2), N(2′), C(8), C(8′) [Ni −0·313, C(9) −0·723]	−0·3044	0·0000	−0·9526	0·0813
Plane (7)	C(8), C(8′), C(9)	0·6135	0·0000	−0·7897	2·2540

Angles between planes (°)

(1)—(2)	161·9	(5)—(6)	13·9
(1)—(3)	161·6	(6)—(7)	55·6
(1)—(4)	161·7		

The molecule has an oblique-puckered[8] conformation (Figure), with a rather large angle of 37° between the aromatic ligand moieties; and associated with this is a symmetrical boat conformation of the six-membered chelate ring containing the trimethylene moiety. The latter is symmetrical with respect to its long axis (crystallographic mirror plane) and the conformation is defined by the angles between planes 5, 6, and 7 of Table 3. Such boat conformations are rare. There

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[7] M. Green and P. A. Tasker, *J. Chem. Soc.* (*A*), 1970, 2531.

[8] M. N. Akhtar, E. D. McKenzie, R. E. Paine, and A. J. Smith, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 673.

appears to be an example in the structure[9] of [VO(saltn)]$_n$, and several distorted ones also have been reported recently.[10]

The same oblique-puckered conformation of the molecule is observed in the known crystal structures of the other compounds of the 'ab' ligands. In [Co(5-Cl-aben)],[11] the angle between aromatic moieties is 29·4°; in [Cu(abpn)] it is 15·2°, a figure which agrees closely with our value[12] of 14·7° for an incompletely refined analysis[1] of the isomorphous [Ni(abpn)]. (The cobalt compound also is isomorphous.[1]) Crystal-packing also is markedly similar in these compounds. The space group is *Pnma* for the compounds [M(abtn)], [Co-(5-Cl-aben)],[11] and [M(aben)];[12] whereas the compounds [M(abpn)] (M = Co, Ni, Cu) are in $P2_12_12_1$, which is a sub-group of the former.

This oblique-puckered conformation of each of these compounds probably does not represent the lowest energy conformation of the isolated molecules. Rather it seems to result in each case from intermolecular forces in the solids. Here we are in opposition to Hall *et al.* in their discussion[13] of the [Cu(abpn)] structure. They seem to be implying that short intermolecular contacts will always be observable when intermolecular forces are constraining the molecule into an unstable conformation. This is not so. Certainly abnormally short contacts are an indication of constraints, but the absence of them does not prove the contrary. The magnitude of the force required to hold an unstable conformation in the solid may be too small to be observable as measurably short intermolecular contacts. This will be particularly so if, as in the [Ni(abtn)] molecule, there is a significant energy barrier to the conversion into other possible isomers.

As observed by Hall *et al.*, there are no abnormally short intermolecular contacts in the crystal structures of [M(abpn)], but the published[11] structure of [Co(5-Cl-aben)] does support our thesis that these molecules are constrained into unstable conformations. The two chlorine substituents of the phenyl rings are not coplanar with the phenyl by 0·13 in a way that suggests conformational constraint.

Also there are other independent lines of evidence which suggest that the isolated molecules adopt conformations different from those observed in the solids.

The ^{1}H n.m.r. spectra of the various nickel(II) species[1,7] show that fast interconversion of conformers is occurring in solution. For example, the two central methylene protons of [Ni(abtn)] [those attached to C(9)] are equivalent, as are the four terminal ones [attached to C(8) and C(8′)], and all four methylene protons of [Ni(aben)] (and substituted analogues) give only a single resonance. This does not define conformation in solution, except that the time-average is symmetrical; but we might expect the rate of interconversion to be slower if the conformation of the solid is the stable one.

We have already noted above the differences of electronic spectra between [Co(abtn)] in the solid and in solution. These differences would have a ready explanation in terms of a conformational change between the two phases, and seem to be much larger than one would expect for solvation phenomena, especially since a very much smaller variation between spectra is observed for solutions in donor and non-donor solvents.

It may also be pertinent that many of these compounds of the N_4 ligand systems tend to crystallise as solvates, in which they may well have a different (and perhaps more stable) conformation.

Thus we favour the view that the observed conformation is not the most stable one for the isolated molecule, but is simply the one which produces a crystalline structure of lowest energy.

[3/2352 *Received*, 16*th November*, 1973]

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[9] M. Mathew, A. J. Carty, and G. J. Palenik, *J. Amer. Chem. Soc.*, 1970, **92**, 3197.

[10] P. R. Ireland, D. A. House, and W. T. Robinson, *Inorg. Chim. Acta*, 1970, **4**, 137; B. W. Skelton, T. N. Waters, and N. F. Curtis, *J.C.S. Dalton*, 1972, 2133.

[11] R. Karlsson, L. M. Engelhardt, and M. Green, *J.C.S. Dalton*, 1972, 2463.

[12] N. A. Bailey and E. D. McKenzie, unpublished data.

[13] D. Hall, T. N. Waters, and P. E. Wright, *J.C.S. Dalton*, 1973, 1508.