Crystal and Molecular Structure of Bis[(*aci*-nitromethyl)benzenato]-(*NNN'N'*-tetramethyl-1,2-diaminoethane)nickel(II)

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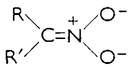
Crystals of the title compound are monoclinic, space group $I2^I$ with a = 12.223(10), b = 7.871(10), c = 21.954(20) Å; β = 90.21(10)°, Z = 4. The structure was determined by the heavy-atom method by use of the intensities of 1 368 independent reflections collected by counter methods, and refined by full-matrix least-squares techniques to R 0.045. The nickel atom is in a six-co-ordinate environment of crystallographic C_2 symmetry. It is bonded to the two nitrogen atoms of the diaminoethane ligand [2.114(4) Å] and to two chelating (*aci*-nitromethyl)benzenato-ions [each having Ni–O 2.085(3) and 2.093(3) Å].

NUMEROUS studies on transition-metal compounds containing co-ordinated nitrite groups have shown that the nitrite group can be nitrogen bonded,[1] chelating,[2] or form a variety of bridges between two metal atoms.[3]



(I)

The nitrate ion also exhibits a range of co-ordination modes.[4] Related to both these ions are the *aci*-nitromethanato-ions (I) formed by the reaction of base with alkyl and aryl nitromethane.

We have taken a number of these anions and investigated their co-ordination chemistry [5] and now report a single-crystal *X*-ray study of bis[(*aci*-nitromethyl)benzenato](*NNN'N'*-tetramethyl-1,2-diaminoethane)nickel(II). The structure was carried out to ascertain unambiguously the mode of bonding of the nitronato-ion.

EXPERIMENTAL

A solution of (*aci*-nitromethyl)benzenato-ions was prepared by the addition of phenylnitromethane to an aqueous sodium hydroxide solution (1 : 2 molar ratio) followed by the

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[1] I. Oonishi, H. Fukimaki, F. Muto, and Y. Komiyama, *Bull. Chem. Soc. Japan*, 1970, **43**, 733.

[2] M. G. B. Drew and D. Rogers, *Chem. Comm.*, 1965, **476**. For complete molecular dimensions, see M. G. B. Drew, Ph.D. Thesis, University of London, 1966.

[3] D. M. L. Goodgame, M. A. Hitchman, and D. F. Marsham, *J. Chem. Soc.* (*A*), 1971, 259.

[4] C. C. Addison, N. Logan, S. C. Wallwork, and C. D. Garner, *Quart. Rev.*, 1971, **25**, 289.

[5] J. A. Cook, Ph.D. Thesis, University of Reading, 1974.

careful addition of dilute hydrochloric acid until pH *ca.* 7. This solution was slowly added to an ethanol–water (1 : 1) solution of nickel(II) nitrate and $(Me_2NCH_2)_2$ (1 : 1 molar ratio) until the nickel to benzenato-ion molar ratio was 1 : 2. When the resulting mixture was set aside overnight green crystals were deposited.

Crystal Data.—$C_{20}H_{28}N_4NiO_4$, $M = 447.1$, Monoclinic, $a = 12.223(10)$, $b = 7.871(10)$, $c = 21.954(20)$ Å, $\beta = 90.21(10)°$, $U = 2\,112.12$ Å^3, $D_c = 1.40$, $Z = 4$, $D_m = 1.40(2)$, $F(000) = 944$. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ (Mo-K_α) = 28.3 cm^{-1}. Space group $I2/c$ from systematic absences: hkl for $h + k + l = 2n + 1$, $h0l$ for $l = 2n + 1$; non-standard setting of No. 15 (C_{2h}^6) with equivalent positions $(0,0,0;\ \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2},) \pm (x,y,z : \tfrac{1}{2}-x,y,-z)$.

A crystal of dimensions 0.15 × 0.35 × 0.70 mm was mounted with the (010) planes perpendicular to the instrument axis of a General Electric XRD 5 apparatus which was used to measure diffraction intensities and cell dimensions (*via* a least-squares treatment of 2θ values of high-angle reflections). The instrument was equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. Zirconium-filtered Mo-K_α radiation was used, with the stationary-crystal–stationary counter method, a 4° take-off angle, and a counting time of 10 s. Individual backgrounds were taken for those reflections whose counts were seriously affected by the streaking of other orders. For other reflections backgrounds were taken from plots of backgrounds *vs.* 2θ. Several standard reflections which were monitored during the course of the experiment showed no significant changes in intensity. No absorption or extinction corrections were applied. Of 1856 independent reflections measured with $2\theta < 50°$, 1368, with $I > 3\sigma(I)$, where the standard deviations $\sigma(I)$ were taken to be $[I + 2E + 0.03I^2]^{\frac{1}{2}}$, and E is the estimated background, were used in the subsequent refinement.

Structure Determination.—The structure was determined from Patterson and Fourier syntheses and refined by full-matrix least-squares. The weighting scheme, chosen to give $w\Delta^2$ for groups of reflections independent of the value of F_o and sinθ/λ, was $\sqrt{w} = 1$ for $F_o < 31$ and $\sqrt{w} = 31/F_o$ for $F_o > 31$. Calculations were made on a CDC 7 600 computer of the University of London Computer Centre, using published programs.[6] Atomic scattering factors used were taken from ref. 7 for hydrogen, and from ref. 8 for nickel, carbon, nitrogen, and oxygen, together with anomalous dispersion corrections for nickel. The anisotropic thermal parameter is defined as $\exp\,(-2\pi^2 \sum_i \sum_j U_{ij}h_ih_jb_ib_j)$ $(i,j = 1,2,3)$ and where b_i is the i'th reciprocal lattice vector. The isotropic thermal parameter is defined as $\exp(-8\pi^2 U\sin^2\theta/\lambda^2)$. The nickel, carbon, nitrogen, and oxygen atoms were refined anisotropically.

A difference-Fourier map was then calculated. The positions of all hydrogen atoms were clearly observed in acceptable positions, and were then included in the least-square refinement with isotropic thermal parameters. The final R value was 0.045. In the final cycle of refinement all shifts were $<0.05\sigma$ and none of the zero reflections showed any serious discrepancy.

Final atomic co-ordinates and thermal parameters, together with standard deviations, are listed in Tables 1 and 2. Final observed and calculated structure factors together with inter- and intra-molecular non-bonding contacts and distances from least-squares planes are listed in Supplementary Publication No. SUP 21398 (8 pp., 1 microfiche).† Bond distances and angles are given in Table 3.

TABLE 1

Final atomic co-ordinates (× 10^4, for hydrogen × 10^3), with estimated deviations in parentheses

Atom	x	y	z
Ni	2 500 [a]	1 634(1)	5 000 [a]
O(1)	2 926(2)	3 436(4)	4 346(1)
O(2)	4 150(2)	2 341(4)	4 977(1)
N(1)	3 962(3)	3 378(5)	4 511(2)
N(2)	2 542(3)	−0 354(5)	4 353(2)
C(1)	4 735(4)	4 225(6)	4 242(2)
C(2)	4 648(3)	5 172(6)	3 677(2)
C(3)	3 735(4)	5 224(7)	3 302(2)
C(4)	3 767(5)	6 067(7)	2 743(2)
C(5)	4 716(5)	6 885(8)	2 570(3)
C(6)	5 631(5)	6 847(8)	2 939(3)
C(7)	5 591(5)	6 007(7)	3 488(3)
C(8)	2 807(4)	−1 916(7)	4 701(3)
C(9)	3 351(6)	−0 141(9)	3 855(3)
C(10)	1 448(5)	−0 501(8)	4 071(3)
H(1)	546(4)	412(6)	444(2)
H(3)	308(4)	466(6)	342(2)
H(4)	312(4)	610(7)	250(3)
H(5)	474(4)	760(8)	218(3)
H(6)	637(4)	757(10)	277(3)
H(7)	621(5)	594(8)	381(3)
H(81)	259(4)	−287(7)	443(2)
H(82)	364(5)	−195(7)	482(3)
H(91)	406(7)	007(12)	404(4)
H(92)	323(6)	−105(12)	350(4)
H(93)	313(5)	090(10)	363(3)
H(101)	143(6)	−158(10)	377(3)
H(102)	126(4)	054(7)	387(2)
H(103)	090(5)	−073(7)	441(3)

[a] Parameter fixed.

TABLE 2

Anisotropic thermal parameters (× 10^3) *

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	30.2(4)	34.7(5)	36.7(5)	0†	3.1(3)	0 †
O(1)	34(1)	51(2)	48(2)	00(1)	−2(1)	4(2)
O(2)	36(1)	47(2)	46(2)	01(1)	−0(1)	10(2)
N(1)	36(2)	41(2)	42(2)	2(2)	−4(1)	1(2)
N(2)	41(2)	50(2)	45(2)	−3(2)	3(2)	−2(2)
C(1)	34(2)	42(2)	43(2)	0(2)	3(2)	2(2)
C(2)	41(2)	33(2)	40(2)	3(2)	5(2)	−1(2)
C(3)	48(3)	46(3)	48(3)	2(2)	5(2)	−1(2)
C(4)	70(4)	55(3)	45(3)	5(3)	−4(3)	1(2)
C(5)	87(4)	63(4)	48(3)	−10(3)	2(3)	17(3)
C(6)	78(4)	67(4)	65(4)	−21(3)	9(3)	11(3)
C(7)	57(3)	54(3)	48(3)	−12(2)	7(2)	6(2)
C(8)	56(3)	43(3)	62(3)	3(2)	−11(2)	−7(2)
C(9)	68(4)	66(4)	58(4)	−9(3)	20(3)	−21(3)
C(10)	61(3)	55(3)	53(3)	−2(3)	−15(3)	−3(3)

* Isotropic thermal parameters for the hydrogen atoms (×10^3) are: H(1) 37(11), H(3) 49(14), H(4) 66(17), H(5) 68(16), H(6) 111(23), H(7) 84(20), H(81) 56(14), H(82) 77(18), H(91) 122(29), H(92) 128(28), H(93) 89(23), H(101) 108(23), H(102) 49(14), H(103) 66(16). † Parameter fixed.

DISCUSSION

The structure consists of discrete units with the nickel atom in a six-co-ordinate environment and the (*aci-*

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† See Notice to Authors No. 7, in *J.C.S. Dalton*, 1974, Index issue.

[6] *X*-Ray System of Programs, July 1972 version, eds. J. C. Baldwin, R. V. Chastain, D. F. High, F. A. Kundell, and J. M. Stewart, University of Maryland Technical Report TR 192.

[7] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

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

nitromethyl)benzenato-groups forming four-membered chelating rings with the metal. The molecule has a crystallographic C_2 axis passing through the nickel atom and the mid-point of the $C(8)-C(8^{\mathrm{I}})$ bond. The molecule is shown in Figure 1 together with the atomic numbering scheme. Hydrogen atoms are numbered such that the first digit refers to the carbon atom to which they are bonded.

TABLE 3

Bond distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances

Ni–O(1)	2.085(3)	C(1)–C(2)	1.450(6)
Ni–O(2)	2.093(3)	C(2)–C(3)	1.386(6)
Ni–N(2)	2.114(4)	C(2)–C(7)	1.391(7)
O(1)–N(1)	1.316(4)	C(3)–C(4)	1.395(7)
O(2)–N(1)	1.328(5)	C(4)–C(5)	1.381(9)
N(1)–C(1)	1.301(6)	C(5)–C(6)	1.380(9)
N(2)–C(8)	1.482(7)	C(6)–C(7)	1.376(8)
N(2)–C(9)	1.486(8)	$C(8)-C(8^{\mathrm{I}})$	1.514(7)
N(2)–C(10)	1.475(7)		

(*b*) Angles

O(1)–Ni–O(2)	63.9(1)	Ni–N(2)–C(9)	115.3(3)
$O(1)-Ni-O(2^{\mathrm{I}})$	94.5(1)	C(8)–N(2)–C(9)	109.1(4)
$O(1)-Ni-O(1^{\mathrm{I}})$	94.3(1)	C(9)–N(2)–C(10)	107.8(4)
O(2)–Ni–N(2)	98.9(1)	C(1)–C(2)–C(3)	125.5(4)
$N(2)-Ni-N(2^{\mathrm{I}})$	84.5(2)	C(1)–C(2)–C(7)	116.1(4)
O(1)–Ni–N(2)	92.0(1)	C(3)–C(2)–C(7)	118.3(4)
$O(1)-Ni-N(2^{\mathrm{I}})$	166.6(1)	N(1)–C(1)–C(2)	126.9(4)
$O(2)-Ni-O(2^{\mathrm{I}})$	149.2(1)	C(2)–C(3)–C(4)	120.8(5)
$O(2)-Ni-N(2^{\mathrm{I}})$	103.8(1)	C(3)–C(4)–C(5)	119.3(5)
O(1)–N(1)–O(2)	113.4(3)	C(4)–C(5)–C(6)	120.5(5)
O(2)–N(1)–C(1)	122.7(3)	C(5)–C(6)–C(7)	119.6(6)
O(1)–N(1)–C(1)	123.9(4)	C(6)–C(7)–C(2)	121.4(5)
Ni–N(2)–C(8)	105.9(3)	Ni–O(1)–N(1)	91.7(2)
Ni–N(2)–C(10)	108.4(3)	Ni–O(2)–N(1)	91.0(2)
C(8)–N(2)–C(10)	110.3(4)	$N(2)-C(8)-C(8^{\mathrm{I}})$	109.8(4)

(*c*) Bond distances for H atoms

C(1)–H(1)	0.99(4)	C(8)–H(81)	1.00(5)
C(3)–H(3)	0.96(5)	C(8)–H(82)	1.05(6)
C(4)–H(4)	0.96(6)	C(9)–H(91)	0.97(8)
C(5)–H(5)	1.02(6)	C(9)–H(92)	1.08(9)
C(6)–H(6)	1.13(7)	C(9)–H(93)	0.99(7)
C(7)–H(7)	1.04(6)	C(10)–H(101)	1.08(8)
		C(10)–H(102)	0.96(5)
		C(10)–H(103)	1.02(6)

(*d*) Angles for H atoms

N(1)–C(1)–H(1)	114(3)	C(6)–C(7)–H(7)	127(4)
C(2)–C(1)–H(1)	119(3)	C(2)–C(7)–H(7)	112(3)
C(2)–C(3)–H(3)	120(3)	$C(8^{\mathrm{I}})-C(8)-H(81)$	113(3)
C(4)–C(3)–H(3)	120(3)	N(2)–C(8)–H(81)	105(3)
C(3)–C(4)–H(4)	119(3)	$C(8^{\mathrm{I}})-C(8)-H(82)$	106(3)
C(5)–C(4)–H(4)	121(3)	N(2)–C(8)–H(82)	111(3)
C(4)–C(5)–H(5)	121(3)	H(81)–C(8)–H(82)	113(4)
C(6)–C(5)–H(5)	118(3)		
C(5)–C(6)–H(6)	117(4)		
C(7)–C(6)–H(6)	124(4)		
N(2)–C(9)–H(91)	109(5)	N(2)–C(10)–H(101)	110(4)
N(2)–C(9)–H(92)	112(4)	N(2)–C(10)–H(102)	110(3)
N(2)–C(9)–H(93)	106(4)	N(2)–C(10)–H(103)	107(3)
H(91)–C(9)–H(92)	123(6)	H(101)–C(10)–H(102)	113(5)
H(92)–C(9)–H(93)	107(6)	H(101)–C(10)–H(103)	107(5)
H(93)–C(9)–H(93)	99(6)	H(102)–C(10)–H(103)	110(4)

Roman numerals as superscripts refer to an atom in the following equivalent positions relative to the reference molecule at x, y, z:

I $\frac{1}{2} - x, y, 1 - z$
II $x, 1 + y, z$
III $1 - x, 1 - y, 1 - z$
IV $1 - x, -y, 1 - z$
V $\frac{1}{2} - x, \frac{3}{2} - y, \frac{1}{2} - z$
VI $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$
VII $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
VIII $\frac{1}{2} + x, 1 - y, z$
IX $\frac{1}{2} + x, -y, z$

Nickel–oxygen [Ni–O(1) 2.085(3) and Ni–O(2) 2.093(3) Å] and nickel–nitrogen [2.114(4) Å] bond lengths formed between the metal and the donor atoms of $(Me_2NCH_2)_2$ are very similar to those in (*NNN′N′*-tetramethyl-1,2-diaminoethane)bis(nitrito)nickel(II) which contains the chelating nitrito-group[2] [Ni–O 2.08(1), 2.17(1), 2.12(1), and 2.05(1), and Ni–N 2.09(1) and 2.07(1) Å].

The angles subtended at the metal ion reveal the distorted nature of the octahedral configuration of the metal (Table 3): O(1) and O(2) of the chelate ring subtend 63.9(1)°, while the nitrogen atoms subtend 84.5(2)°. The atoms approximately *trans* to each other [O(1) and $N(2^{\mathrm{I}})$, and O(2) and $O(2^{\mathrm{I}})$] subtend at the metal angles of 166.6(1) and 149.2(1)° respectively. All the angles subtended at the metal are within 6° of those found in $[Ni(NO_2)_2\{(Me_2NCH_2)_2\}]$.[2]

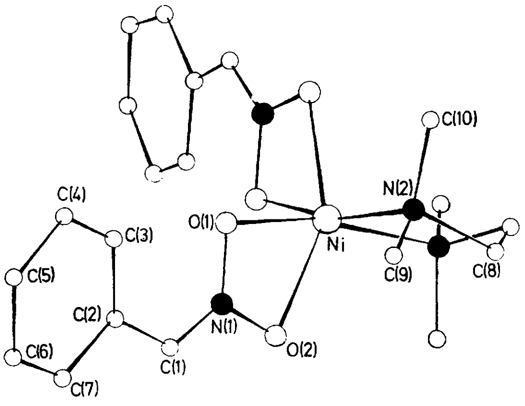

FIGURE 1 The molecule

The four atoms forming the nitronato-chelate ring are planar. The N(1)–O(1) and N(1)–O(2) distances [1.316(4) and 1.328(5) Å] and the O(1)–N(1)–O(2) angle [113.4(3)°] are similar to those for the chelating *aci*-nitro-group in bis(2-*aci*-nitropropanato)copper(II) where the N–O distances are 1.32(3) and 1.37(5) Å,* and the angle is 110(2)°.[9] The N–O bond lengths reported here and previously [9] for the nitronato-ions are longer than those reported [1.26(2) and 1.25(2) Å][2] for the chelating nitrito-ion. This lengthening of the N–O bond is probably caused by electron-withdrawal by the adjacent formal double-bond between C(1) and N(1). The C(1)–N(1) distance [1.301(6) Å] is indeed longer than that [1.28 Å] usually associated with a carbon–nitrogen double-bond.[10,11] In bis(*aci*-nitropropanato)copper(II) the comparable bond [1.35(4) Å] is longer than the present one, but this difference may not be significant.

The C(1)–C(2) bond length [1.450(6) Å] is shorter than

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* It is not clear from ref. 9 why the standard deviations are so variable.

[9] O. Simonsen, *Acta Cryst.*, 1973, **B29**, 2600.

[10] H. L. Ammon, *Acta Cryst.*, 1974, **B30**, 1731.

[11] J. Iball and W. S. Motherwell, *Acta Cryst.*, 1969, **B25**, 882.

expected (1.475 Å)[12] for a single bond between two carbon atoms where both are in a trigonal planar environment. It is however comparable in length (1.436 Å) to a single carbon–carbon bond reported between two trigonal-planar carbon atoms where one is also bound by a double bond to another carbon atom and the other forms a double bond to a nitrogen atom.[13]

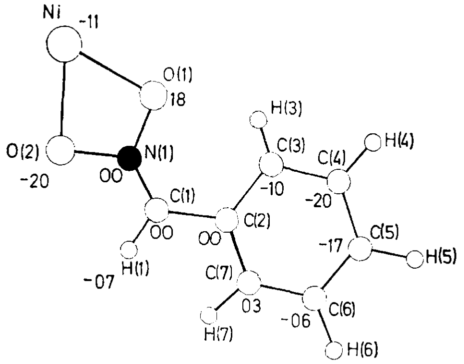

FIGURE 2 The (*aci*-nitromethyl)benzenato-ligand, together with distances (Å × 10^2) of atoms from the plane of atoms N(1), C(1), and C(2)

The length of the C(1)–C(2) bond suggests there is considerable electron delocalisation into it from the C(1)–N(1) bond and from the phenyl ring. This suggestion is supported by the fact that the plane of the phenyl ring intersects that of the *aci*-nitro-chelate ring at only 15° (Table 4). Because of steric effects it is unlikely that this angle could be less than 15° (Figure 2). As it is, C(1) is 0.10 Å out of the plane of the benzene ring and —0.08 Å from the plane of the *aci*-nitro-group. In addition these two rings are twisted about the Ni · · · N-(1) and C(2) · · · C(5) axes respectively such that O(2) and C(3) are on one side and O(1) and C(7) the other. Thereby interactions between C(7) and H(1), H(7) and H(1), and O(1) and H(3) are decreased, the non-bonding distances being 2.57(4), 2.20(8), and 2.25(5) Å.

All C–C and C–H bond lengths and angles found in $(Me_2NCH_2)_2$ and the phenyl ring are as expected.[2,14] The N–C–C–N torsion angle is —56.4°. The hydrogen atoms on C(9) and C(10) are staggered with respect to C(10) and C(9), C–N–C–H torsion angles being within 15° of ±60 and 180°. Intermolecular contacts show that the molecules are held together in the crystal by the normal van der Waals forces.

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[12] D. R. Lide, *Tetrahedron*, 1962, **17**, 125.

[13] M. Mathew and G. Palenik, *Acta Cryst.*, 1971, **B27**, 59.

[14] O. Bastiansen and M. Traetteberg, *Tetrahedron*, 1962, **17**, 147.