Crystal and Molecular Structure of the 1 : 2 Addition Complex of Bis(phenyldithioacetato)nickel(II) with Pyridine

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Crystals of the title compound [Ni(PhCH$_2$·CHS$_2$)$_2$(py)$_2$] are monoclinic, space group $C2/c$, unit-cell dimensions a = 16.733(10), b = 10.853(5), c = 17.222(10) Å, β = 124.0(1)°, Z = 4. The crystal and molecular structure was determined from photographic X-ray data by the heavy atom method and refined by least squares to R 0.054. The monomeric unit consists of a distorted octahedron about the Ni atom which is situated on a two-fold axis. The pyridine molecules are *cis*-co-ordinated. I.r. and visible spectra are reported.

NICKEL(II) complexes of dithiocarboxylate ligands form pseudo-octahedral addition complexes with neutral molecules which are electron donors.

We have previously determined the crystal structure of tetrakis(phenyldithioacetato)dinickel(II)[1] which shows evidence for the presence of a nickel–nickel bond in a bridging binuclear structure. In order to study the behaviour of the phenyldithioacetato-group as a ligand in a high-spin nickel(II) complex we have undertaken the X-ray structure determination of the bis-adduct of bis(phenyldithioacetato)nickel(II) with pyridine.

EXPERIMENTAL

The compound was prepared as described in ref. 2. Crystals were dark brown prisms developed along the c axis,

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[1] M. Bonamico, G. Dessy, and V. Fares, *Chem. Comm.*, 1969, 1106.

[2] H. Krebs, E. F. Weber, and H. Fanhender, *Z. anorg. Chem.*, 1954, **276**, 128.

rather unstable in air and to X-rays, so that a number of crystals had to be used for data collection.

The room-temperature solid-state magnetic moment is 3.13 B.M. (Gouy method).

Electronic Spectrum.—Pyridine solution, (kK, molar extinction coefficients in parentheses): 9.21sh (24), 10.30 (35), 16.12 (141), 21.93 (198). Solid-state reflection: 9.17, 10.10, 16.26, 21.50 kK.

I.r. Spectrum.—(Nujol mull): 1 382sh,s, 1 376s, 1 365sh,m, 1 350m, 1 270m, 1 231w, 1 215s, 1 192s, 1 176m, 1 165w, 1 148m, 1 105vs, 1 078vs, 1 063vs, 1 040s, 1 028m, 1 010vs, 998s, 976s, 965w, 940m, 909m, 870sh,m, 860vs, 840s, 800m, 760s, 750vs, 700vs, 671w, 656vs, 650sh,m, 655s, 590s, 482s, 462m, 430s, 428sh,m, 388w, 368s, 255s, 222s cm^{-1}.

Crystal Data.—$C_{26}H_{24}N_2NiS_4$, $M = 551.44$, Monoclinic, $a = 16.733(10)$, $b = 10.853(5)$, $c = 17.222(10)$ Å, $\beta = 124.00(17)°$, $U = 2\,593$ Å^3, $D_m = 1.41(2)$ g cm^{-3} (by flotation), $Z = 4$, $D_c = 1.41$ g cm^{-3}, $F(000) = 1\,124.24$. Space group $C2/c$ from systematic absences.

Intensity Measurements.—Unit-cell dimensions were determined by a modified, improved version of Christ's method [3] from a zero-layer Weissenberg film taken about the c axis and precession photographs taken about the b axis by use of reflections from Cu-K_α radiation and, where possible, from Cu-$K_{\alpha 1}$ radiation ($\lambda = 1.540\,56$ Å).

Intensities were estimated visually from sets of multiple-film equi-inclination Weissenberg photographs taken about the c axis for the layers $hk0$—8. The intensities of 791 independent reflections above film background (*ca.* 27% of those possible with Cu-K_α radiation) were collected. Data were corrected for Lorentz and polarization effects and for spot extension. No absorption or extinction corrections were applied. Initial scaling was based on the relative exposure times of the different photographs. Independent layer-scales were refined during the isotropic phase of structure refinement.

Structure Determination.—As there are eight general positions in the space group, the four molecules must each possess a centre of symmetry or a two-fold axis. The interpretation of the Patterson synthesis indicated that the special Ni position is on a two-fold axis at $0,y,1/4$. The Patterson synthesis also enabled the positions of the sulphur atoms and of the nitrogen atom to be determined. Thereafter, standard Fourier methods were used to locate the other atoms (except hydrogen) and to achieve a further improvement of the atomic parameters. The R value at this stage was 0.20. Five cycles of 4 × 4 block-diagonal least-squares refinement of all atomic positional and isotropic thermal parameters reduced R to 0.084. The hydrogen atoms of the phenyl group and of the pyridine molecule were then included at calculated positions assuming C–H 1.00 Å and with isotropic temperature factors fixed at 4.5 Å^2. Further refinement of non-hydrogen atomic parameters reduced R to 0.083. The refinement was then continued for all non-hydrogen atoms by use of anisotropic thermal parameters with a 9 × 9 diagonal approximation. The weighting scheme used was $w = [a + bF_o + cF_o^2]^{-1}$ with $a = 5.00$, $b = 1.00$, and $c = 0.0025$. The final R value was 0.054.[*] Table 1 gives final atomic parameters. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21687 (6 pp., 1 microfiche).[†] Bond distances and angles within the crystal chemical unit are listed in Table 2. The Figure shows a projection of the structure.

Calculations.—Calculations were carried out on a Univac 1108 computer at Rome University. Intensity corrections, scaling, Wilson plot, Fourier synthesis, and interatomic distances and angles were calculated by use of programs by Domenicano and Vaciago,[4] and for structure-factors, least-squares planes calculations, and least-squares refinement, by Spagna and Carruthers. Neutral atomic

TABLE 1

Atom co-ordinates (× 10^4) and anisotropic temperature factors,[*] with standard deviations in parentheses

	x/a	y/b	z/c	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Ni	0(0)	541(2)	2 500(0)	48(1)	0(0)	60(2)	99(2)	0(0)	52(2)
S(1)	143(2)	−1 051(2)	1 576(2)	53(1)	−3(3)	61(3)	115(2)	−14(3)	60(3)
S(2)	1 717(2)	195(2)	3 187(2)	54(1)	−14(3)	66(3)	131(2)	−26(4)	67(2)
N	210(5)	1 918(6)	3 457(6)	66(5)	−7(9)	90(11)	98(7)	−23(10)	62(9)
C(1)	1 334(6)	−823(7)	2 302(7)	58(5)	−2(9)	75(10)	99(7)	24(12)	47(8)
C(2)	2 046(6)	−1 469(8)	2 152(8)	63(5)	39(10)	99(13)	109(9)	20(14)	88(10)
C(3)	2 476(6)	−521(7)	1 849(8)	50(5)	10(10)	75(11)	99(8)	−18(13)	66(10)
C(4)	1 958(7)	−86(10)	952(9)	59(7)	−3(13)	65(13)	176(13)	−4(19)	79(11)
C(5)	2 306(9)	852(10)	668(9)	103(8)	59(17)	123(17)	177(14)	61(19)	72(11)
C(6)	3 218(9)	1 316(9)	1 310(11)	102(9)	−21(15)	180(20)	130(11)	12(20)	139(15)
C(7)	3 751(7)	872(9)	2 201(10)	72(7)	−67(14)	106(15)	141(11)	−73(19)	116(13)
C(8)	3 370(6)	−41(8)	2 465(8)	55(5)	4(11)	63(11)	143(10)	−41(15)	65(9)
C(9)	−293(7)	1 997(8)	3 842(8)	72(6)	19(12)	83(13)	114(9)	5(14)	58(10)
C(10)	−98(8)	2 781(8)	4 550(8)	100(8)	49(14)	118(16)	121(10)	9(15)	56(11)
C(11)	687(8)	3 561(8)	4 895(8)	103(9)	9(14)	86(16)	111(9)	−18(15)	64(11)
C(12)	1 207(8)	3 525(9)	4 497(9)	99(8)	−47(14)	79(16)	123(10)	−28(17)	72(12)
C(13)	946(7)	2 701(8)	3 780(9)	87(7)	−39(12)	115(15)	112(9)	−38(16)	83(11)

	x/a	y/b	z/c		x/a	y/b	z/c
H(2,1)	2 568	−1 863	2 750 [†]	H(8)	3 760	−356	3 123
H(2,2)	1 704	−2 113	1 656	H(9)	−860	1 435	3 592
H(4)	1 311	−451	488	H(10)	−506	2 792	4 808
H(5)	1 907	1 183	14	H(11)	873	4 138	5 423
H(6)	3 486	1 982	1 118	H(12)	1 769	4 090	4 724
H(7)	4 412	1 201	2 661	H(13)	1 324	2 691	3 491

[*] In the form: $T = \exp[-10^{-4}(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$. [†] All hydrogen atoms have B 4.5 Å^2 (see text).

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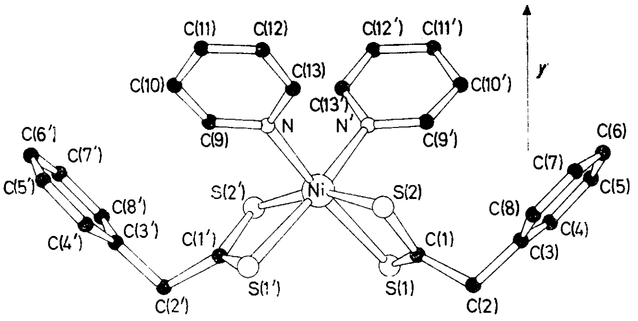
[*] Since the crystals used for data collection are unstable to X-rays, we were able to collect only 27% of the possible reflections as mentioned in the text. Consequently, the apparent high accuracy of our results is probably limited.

[†] See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

[3] G. Mazzone, A. Vaciago, and M. Bonamico, *Ricerca sci.*, 1963, **33**, (IIA), 1113.

[4] A. Domenicano and A. Vaciago, unpublished work.

scattering factors, corrected for anomalous dispersion in the case of nickel and sulphur atoms,[5] were taken from ref. 6.



A projection of the structure

Table 2

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

(*a*) Distances

Ni–S(1)	2.449(3)	C(3)–C(8)	1.36(1)
Ni–S(2)	2.448(2)	C(4)–C(5)	1.39(2)
Ni–N	2.10(1)	C(5)–C(6)	1.39(2)
S(1)–C(1)	1.68(1)	C(6)–C(7)	1.36(2)
S(2)–C(1)	1.69(1)	C(7)–C(8)	1.38(2)
N–C(9)	1.33(2)	C(9)–C(10)	1.37(2)
N–C(13)	1.34(1)	C(10)–C(11)	1.39(2)
C(1)–C(2)	1.52(2)	C(11)–C(12)	1.38(2)
C(2)–C(3)	1.51(2)	C(12)–C(13)	1.38(2)
C(3)–C(4)	1.36(2)		

(*b*) Angles

S(1)–Ni–S(2)	72.0(1)	C(2)–C(3)–C(8)	121(1)
S(1)–Ni–N	167.4(2)	C(4)–C(3)–C(8)	118(1)
S(2)–Ni–N	95.4(2)	C(3)–C(4)–C(5)	121.7(8)
Ni–S(1)–C(1)	85.4(4)	C(4)–C(5)–C(6)	118(1)
Ni–S(2)–C(1)	85.0(3)	C(5)–C(6)–C(7)	120(1)
Ni–N–C(9)	124.0(5)	C(6)–C(7)–C(8)	119.5(9)
Ni–N–C(13)	119.0(1)	C(3)–C(8)–C(7)	122(1)
S(1)–C(1)–S(2)	117.5(7)	N–C(9)–C(10)	126(1)
S(1)–C(1)–C(2)	121.5(7)	C(9)–C(10)–C(11)	117(1)
S(2)–C(1)–C(2)	121.0(5)	C(10)–C(11)–C(12)	119(1)
C(1)–C(2)–C(3)	108.4(7)	C(11)–C(12)–C(13)	119(1)
C(2)–C(3)–C(4)	120.3(8)	N–C(13)–C(12)	123(1)

DISCUSSION

The crystal structure consists of discrete monomeric units. The nickel atom is in a *cis*-distorted octahedral environment consisting of four sulphur atoms from two phenyldithioacetato-groups and two nitrogen atoms from two pyridine molecules. The two phenyldithioacetato-ligands chelate to the same nickel atom thus forming four-membered rings. The behaviour of the ligand is thus very different from that observed in tetrakis(phenyldithioacetato)dinickel(II).[1] As we have previously observed,[7] the formation of four-membered chelate rings in the metal complexes causes some deformations in the co-ordination angles of the metal atom and in the valence angles of the atoms forming the ring. In square-planar nickel(II) complexes with sulphur-donor ligands, it seems that an extensive molecular conjugation and consequent electron delocalization can lead to the formation of four-membered chelate complexes. This effect is evident in the chelated dithiobenzoate nickel(II) complex,[8] which is a planar conjugated molecule. In tetrakis(phenyldithioacetato)dinickel(II), extensive conjugation is not possible because of the presence of the CH_2 group; chelate rings are not therefore formed and the ligand molecules bridge two different metal atoms. It is found that structural changes occur in the chelate ring when ligands are added to the metal ion. In the low-spin planar nickel chelate, bis(*OO'*-diethyl phosphorodithioato)nickel(II), when two pyridine molecules are added to form a high-spin *trans*-bis-addition complex the Ni–S distances and the S–P–S angles are increased.[9] Similar structural changes occur when two pyridine molecules are added to bis(phenyldithioacetato)nickel(II) to form a *cis*-bis-addition complex. The Ni–S bond distances increase from 2.20 Å (mean for square-planar Ni^{II} complexes) to 2.45 Å and the S–C–S angles increase from 111 [the mean for bis(dithiobenzoato)nickel(II)] to 117°. These structural changes reduce the strain within the chelate ring and determine the behaviour of phenyldithioacetic acid as a chelating ligand. The addition of ligands to planar metal chelates generally gives *trans*-octahedral complexes.

The *cis*-configuration observed in the present bis-pyridine addition complex is unusual and some structural changes can be expected from this configuration. In particular, the two chelate rings are no longer coplanar and, consequently, the Ni–S bond distances (2.45 Å) are shorter than those in the *trans*-bis-addition complexes [2.50 Å in the bis-pyridine addition complex of bis(diphenyldithiophosphinato)nickel(II) [10] and 2.49 Å in that of bis(*OO'*-diethyl phosphorodithioato)nickel(II)]; they are, however, in the range of Ni–S distances found in high-spin nickel complexes. The value of the nickel–nitrogen bond length (2.104 Å) is in agreement with those in analogous six-co-ordinate compounds. All other bond distances are as expected. The mean sulphur–carbon bond length (1.68 Å) is similar to the distances observed in similar four-membered chelate rings. The C(1)–C(2) and C(2)–C(3) distances have values accepted for C–C single bonds. The bond distances and angles related to the phenyl groups and the pyridine molecule are all as expected.

The electronic spectrum is typical of high-spin pseudo-octahedral nickel(II) complexes. The first band, centred at 9.75 kK with two components at 9.21 and 10.30 kK, may be assigned to $^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)$ in O_h. The other two bands at 16.12 and 21.93 kK can be similarly assigned to $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$ and $^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)$ respectively.[11] The splitting of the first band seems too large (>1 kK) in comparison with analogous results for *trans*-octahedral pyridine addition complexes containing the chromophore $[NiS_4N_2]$, *e.g.* $[Ni(S_2PPh_2)(py)_2]$.[10] This fact can be explained as a result of the different electronic properties of the dithiocarboxylate

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[5] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[6] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 324.

[7] M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *J.C.S. Dalton*, 1972, 2515.

[8] M. Bonamico, G. Dessy, and L. Scaramuzza, *J.C.S. Dalton*, 1975, 2250.

[9] S. Ooi and Q. Fernando, *Inorg. Chem.*, 1967, **6**, 1558.

[10] P. Porta, A. Sgamellotti, and N. Vinciguerra, *Inorg. Chem.*, 1971, **10**, 541.

[11] A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' Elsevier, Amsterdam, 1968.

and dithiophosphate ligands; the markedly different behaviour of these two types of ligands, both in stereochemistry and electronic spectra, has also been noted in chromophores of the type [NiS_4].[12]

The i.r. spectrum is expected to be complicated by the presence of different rings. The far-i.r. region is the most interesting and diagnostic of the stereochemistry of the complex, since this is the region where the stretching frequencies ν(Ni–py) are found. Two bands are expected in a *cis*-octahedral complex (a_1 and b_1 in C_{2v} symmetry) both i.r.-active,[13] and these can be assigned to the bands at 255 and 222 cm^{-1}. The stretching vibrations of the metal and co-ordinated pyridine are as expected in the region 287—200 cm^{-1}.[13]

[5/1987 *Received, 13th October*, 1975]

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[13] R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, 1965, **4**, 350.