Notes

Chemical and Structural Investigations on Bismuth Complexes of 2,6-Diacetylpyridine Bis(2-thenoylhydrazone) and 2,6-Diacetylpyridine Bis(thiosemicarbazone)†

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Bismuth complexes with the polydentate ligands 2,6-diacetylpyridine bis(2-thenoylhydrazone) (H_2dapt) and 2,6-diacetylpyridine bis(thiosemicarbazone) (H_2dapts) were synthesized and characterized by means of i.r. spectroscopy and *X*-ray crystal analysis. In the complex [Bi(dapt)(OH)]·dmso·H_2O (**1**) (dmso = dimethyl sulphoxide) the co-ordination of the carbonyl and azomethine groups is in agreement with the shift of the amide I and II bands to lower and higher frequencies respectively. For [Bi(dapts)(N_3)]·0.5dmso (**2**) the strong band at 2 025 cm^{-1} is in accord with co-ordination of the azide group, and involvement of the sulphur atom in the co-ordination is evidenced by the negative shift of the band from 1 250 to 1 180 cm^{-1}. The crystals of (**1**) and (**2**) are monoclinic, space group $P2_1/n$, with lattice constants: (**1**), a = 14.763(7), b = 10.844(6), c = 16.590(7) Å, β = 105.03(3)°, Z = 4, and R = 0.0483; (**2**) a = 21.112(9), b = 11.939(7), c = 7.333(6) Å, β = 97.86(6)°, Z = 2 for a double formula, and R = 0.0546. In both compounds the geometry around bismuth is pentagonal pyramidal with the base occupied by the organic ligand and the apical site occupied by the OH^- and N_3^- groups for (**1**) and (**2**) respectively.

The chelating properties of polyfunctional organic ligands, containing the C(O)NH or C(S)NH moieties have been intensively investigated in recent years in our laboratories.[1–4] In particular, 2,6-diacetylpyridine acylhydrazones revealed a variety of different conformations and configurations, in connection with the nature of the metal and the counter ion.[4–6] Recently, the ligand behaviour of 2,6-diacetylpyridine bis(2-thenoylhydrazone) (H_2dapt) has been investigated in two bismuth(III) complexes[7] for which *X*-ray analysis revealed interesting chemical and structural aspects concerning the stereochemistry and the deprotonated nature of the hydrazone. As an extension of this research programme, we now report the synthesis, the i.r. spectra, and the *X*-ray analysis of two new bismuth(III) complexes obtained by the reaction of $BiCl_3$ with H_2dapt and 2,6-diacetylpyridine bis(thiosemicarbazone) (H_2dapts).

Experimental

Materials and Preparations.—Bismuth trichloride, 2,6-diacetylpyridine, 2-thiophenecarbohydrazide, and thiosemicarbazide were used as received without further purification. 2,6-Diacetylpyridine bis(2-thenoylhydrazone) (H_2dapt) and 2,6-diacetylpyridine bis(thiosemicarbazone) (H_2dapts) were obtained as previously reported.[5,8] Infrared spectra (4 000—200 cm^{-1}) for KBr discs were recorded on a Perkin-Elmer 283B spectrophotometer.

[Bi(dapt)(OH)]·dmso·H_2O (**1**). Bismuth trichloride (1 mmol, 0.315 g) was added to an acetone suspension of H_2dapt (1 mmol, 0.411 g). After stirring for 30 min at room temperature, an excess of pyridine was added dropwise and the solution colour turned from yellow to orange. The filtered solution was taken to dryness under reduced pressure. The resulting substance was then dissolved in dimethyl sulphoxide (dmso) and an aqueous solution (22 cm^3) of imidazole (1 mol, 1.36 g) was added. After several days orange prismatic crystals were formed (Found: C, 34.4; H, 3.5; N, 9.5; S, 13.2. Calc. for $C_{21}H_{24}Bi_2N_5O_5S_3$: C, 34.4; H, 3.4; N, 9.6; S, 13.1%).

[Bi(dapts)(N_3)]·0.5dmso (**2**). Starting from an acetone suspension of H_2dapts (1 mmol, 0.309 g) and adding $BiCl_3$ (1 mmol, 0.315 g), a yellow solution was obtained which, without filtration, was taken to dryness. After dissolving the obtained powder in dmso, an excess of NaN_3 (2 mmol, 1.3 g) was added. After a few days dark red prismatic crystals were formed (Found: C, 24.4; H, 2.9; N, 23.5; S, 13.6. Calc. for $C_{24}H_{32}Bi_2N_{20}OS_5$: C, 24.2; H, 2.7; N, 23.5; S, 13.5%).

Data Collection, Solution and Refinement of the Structures.—Crystal data and details concerning the data collection are quoted in Table 1; the intensity data after the usual reduction were put on absolute scale by least squares. The structures were solved by the heavy-atom method and refined by full-matrix least-squares cycles using anisotropic thermal parameters for Bi and S atoms and isotropic for the others; in both structures hydrogen atoms were placed at the calculated positions and introduced in the last refinement cycle as fixed contributors. For compound (**2**) 28 reflections which could be affected by extinction or counting errors were suppressed before the last refinement cycle; Tables 2 and 3 report the final atomic coordinates for (**1**) and (**2**) respectively. In both compounds the dmso molecule is disordered: in (**1**) the sulphur atom is localized at two positions with occupancy factor 0.5; in (**2**) the molecule is disordered around a symmetry centre. Some disorder also involves the carbon and sulphur atoms on the thiophene rings of (**1**) (atoms A and B). The atomic scattering factors used, corrected for anomalous dispersion, were from ref. 9; the

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† *Supplementary data available* (No. SUP 56790, 2 pp.): i.r. data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Experimental data* for crystallographic analyses of compounds (**1**) and (**2**)

	(**1**)	(**2**)
M	731.22	1 194.91
a/Å	14.763(7)	21.112(9)
b/Å	10.844(6)	11.939(7)
c/Å	16.590(7)	7.333(6)
α/°	90	90
β/°	105.03(3)	97.86(6)
γ/°	90	90
U/Å^3	2 565(2)	1 831(2)
Z	4	2
D_c/g cm^{-3}	1.894	2.167
D_m/g cm^{-3}	1.93	2.18
Reflections for lattice parameters		
number	15	16
θ range	14—18	10—15
F(000)	1 424	1 140
Crystal size/mm	0.13 × 0.33 × 0.81	0.71 × 0.58 × 0.78
μ/cm^{-1}	71.27	98.96
Scan speed/° min^{-1}	4.5	3.0—6.0
Scan width/°	1.80	1.2 + 0.35 tanθ
θ range	3—22	3—23
h range	$\pm$15	$\pm$23
k range	0—11	0—12
l range	0—17	0—9
Standard reflection	2 5 2	−4 5 2
Maximum intensity variation/%	3.3	3.5
No. of measured reflections	3 479	2 940
No. of reflections used in the refinement	2 247	1 357
Absorption correction (minimum–maximum)	1.00, 2.34	1.00, 1.65
No. of refined parameters	318	129
$R = \Sigma\lvert\Delta F\rvert/\Sigma F_o\lvert$	0.0483	0.0546
$R' = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{\frac{1}{2}}$	0.0469	0.0574
k, g in $w = k[\sigma^2(F_o) + gF_o^2]^{-1}$	1.0, 3.79 × 10^{-4}	2.05, 1.12 × 10^{-3}

* Details in common: space group $P2_1/n$; 293 K; Philips PW 1100 diffractometer; scan mode ω—2θ; criterion for observed reflections, $I > 3\sigma(I)$.

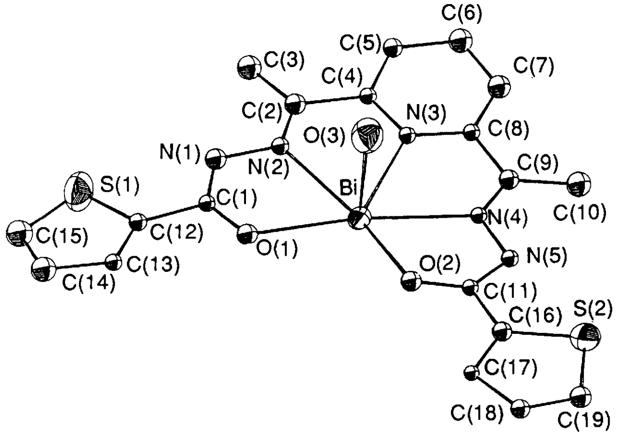


Figure 1. Perspective view of the [Bi(dapt)(OH)] molecule

calculations were performed on a GOULD 32/77 computer using the SHELX 76,[10] ORTEP,[11] and PARST[12] programs.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Discussion

Infrared Spectra.—The spectroscopic pattern of the bideprotonated hydrazone in (**1**) is very similar to that previously observed in [Bi(dapt)Cl]•dmso[7] (**3**) and in other transition-metal complexes of formula M(dapt)•nH$_2$O (M = Co, Ni, Cu, or Zn).[5] In particular, the amide I (1 640 cm^{-1}) and II (1 510 cm^{-1}) bands shift to lower (1 575 cm^{-1}) and higher (1 525 cm^{-1}) frequency values respectively, in agreement with co-ordination of the carbonyl oxygen and azomethine nitrogen atoms.[13,14] As regards the spectra of H$_2$dapts and compound (**2**) the following statements can be made: (*a*) the strong band at 2 025 cm^{-1} is in accord with a co-ordinated azide group; (*b*) a decrease in the number of absorptions in the ν(NH) region (3 500—3 100 cm^{-1}) is observed, as a consequence of the bideprotonated nature of the ligand; (*c*) the participation of both sulphur atoms in the co-ordination to bismuth is evidenced by the negative shift of the strong band from 1 250 to 1 180 cm^{-1}.[3,15] For both complexes the assignments of the S=O stretching vibrations due to solvated dimethyl sulphoxide, which usually occur in the range 1 055—1 010 cm^{-1} for uncomplexed molecules,[16] is complicated by the aromatic ring vibrations.

Structural Considerations.—A view of the [Bi(dapt)(OH)] complex molecule (**1**) is shown in Figure 1: bismuth is six-co-ordinated with a pyramidal-pentagonal geometry in which the apex is occupied by one OH group and the base by nitrogen and oxygen atoms of the ligand which is doubly deprotonated and symmetrically chelated. This situation is similar to the closely related [Bi(dapt)Cl]•dmso[7] (**3**) structure: bond distances and angles involving these molecules are reported in Table 4 for comparison. It can be seen that these values are in very good agreement (except, of course, for the apical bonds); the presence of Cl and OH at the apical site seems not to influence the values of the bond distances and angles of the base of the pyramid. The values of the Bi–N bond distances in several bismuth complexes were considered in a previous work:[17] they fall in the range 2.35(1)—2.90(1) Å, and our results appear at the lower end. The apical Bi–O bond [2.08(1) Å] is considerably shorter than the sum of the covalent radii (2.19 Å) indicative of a strong interaction. In these pyramidal complexes the apical bonds are stronger than the others; this fact could be explained either by considering that these sites are less hindered than the basal ones or that the absence of a ligand in the *trans* position is the cause of a lack of *trans* influence. The present value is comparable to some Bi–O bonds found in the literature, *i.e.* 2.062(14) and 2.065(15) Å in μ-oxo-bis[triphenylbismuth(V)] perchlorate,[18] 2.10(2) and 2.12(2) Å in [Bi$_6$(H$_2$O)(NO$_3$)O$_4$(OH)$_4$][NO$_3$]$_5$,[19] and 2.08(4), 2.11(3), and 2.13(6) Å in [Bi$_6$O$_4$(OH)$_4$][NO$_3$]$_6$•4H$_2$O.[20] The belt of atoms around bismuth are only roughly planar, the donor atoms showing small displacements from their mean plane [maximum deviations 0.08(1) Å for O(1) and N(2)]. The metal lies 0.218(1) Å from this plane and the angles of bismuth involving the OH group are in the range 80.9(4)—87.1(4)°. The molecules are packed by formation of dimers weakly bonded by interactions of type Bi $\cdots$ S(1A$^{\text{I}}$) (I $1 - x$, $1 - y$, $1 - z$) 3.499(6) Å and Bi $\cdots$ N(1$^{\text{I}}$) 3.49(1) Å. These are held together by short contacts (or hydrogen bonds): O(3) $\cdots$ O(1D$^{\text{II}}$) (II $\frac{1}{2} + x$, $\frac{1}{2} - y$, $z - \frac{1}{2}$) 2.83(2), O(3) $\cdots$ O 2.72(2), and N(4) $\cdots$ O(1D$^{\text{II}}$) 3.15(2) Å involving the dmso molecule, water molecule, and the OH group.

The complex molecule [Bi(dapts)(N$_3$)] (**2**) (Figure 2) shows a pyramidal co-ordination as found in (**1**), having in the base plane N(2), N(3), N(4), S(1), and S(2) atoms and the N(8) atom of the azide at the apex. The donor atoms of the pentagonal girdle deviate considerably from planarity: S(1) −0.048(8), N(2) −0.215(18), N(3) 0.053(19), N(4) −0.174(19), and S(2) 0.038(8) Å; the metal lies out of the best plane through these atoms

Table 2. Atomic co-ordinates (× 10^4) for compound (**1**)*

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Bi	6 374.6(5)	3 450.3(6)	4 541.5(4)
S(1A)	2 688(4)	5 941(6)	3 334(4)
S(2)	10 417(4)	2 932(7)	4 703(5)
S(1D)	2 998(9)	5 458(13)	8 588(8)
S(2D)	2 613(9)	5 129(12)	7 954(8)
S(1B)	4 077(0)	6 781(0)	2 713(0)
O(1)	5 262(9)	4 778(11)	3 587(7)
O(2)	7 766(9)	3 912(12)	4 100(8)
O(3)	6 022(9)	2 285(11)	3 511(7)
O(1D)	2 134(11)	4 855(16)	8 584(11)
O	4 614(15)	2 559(21)	2 090(13)
N(1)	4 079(10)	4 181(12)	4 192(9)
N(2)	4 708(10)	3 279(14)	4 600(8)
N(3)	6 033(9)	1 725(12)	5 365(8)
N(4)	7 704(10)	2 046(14)	5 062(8)
N(5)	8 560(10)	2 326(15)	4 916(10)
C(1)	4 465(13)	4 865(15)	3 703(10)
C(2)	4 468(12)	2 548(18)	5 126(11)
C(3)	3 537(13)	2 626(21)	5 342(14)
C(4)	5 189(12)	1 612(15)	5 515(9)
C(5)	4 965(12)	666(17)	5 982(10)
C(6)	5 660(14)	−217(18)	6 317(12)
C(7)	6 555(14)	−103(16)	6 153(10)
C(8)	6 723(12)	859(16)	5 685(10)
C(9)	7 628(12)	1 082(17)	5 517(11)
C(10)	8 456(14)	169(17)	5 843(12)
C(11)	8 506(13)	3 291(20)	4 415(14)
C(12)	3 802(12)	5 796(17)	3 256(11)
C(13A)	4 068(18)	6 771(21)	2 699(15)
C(14)	3 225(16)	7 545(20)	2 442(12)
C(15)	2 486(16)	7 203(20)	2 711(11)
C(16)	9 398(13)	3 690(20)	4 228(13)
C(17)	9 499(11)	4 658(20)	3 697(14)
C(18)	10 462(17)	4 781(26)	3 737(17)
C(19)	11 016(18)	3 966(26)	4 191(16)
C(13B)	2 688(0)	5 951(0)	3 330(0)
C(1D)	2 731(18)	6 864(24)	7 970(16)
C(2D)	3 814(26)	4 739(36)	8 231(24)

* A and B in the thiophene ring correspond to population parameters 0.8 and 0.2 respectively; D is related to the dmso molecule.

Table 3. Atomic co-ordinates (× 10^4) for compound (**2**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Bi	3 768.8(5)	2 595.1(7)	6 686.4(15)
S(1)	4 518(4)	1 432(6)	9 342(12)
S(2)	2 915(3)	942(5)	6 832(11)
S(3)	4 957(10)	629(13)	4 073(22)
O(1)	4 849(23)	1 724(38)	4 972(69)
N(1)	5 326(10)	3 189(16)	8 693(29)
N(2)	4 783(9)	3 738(14)	7 860(25)
N(3)	3 747(10)	4 594(16)	5 988(26)
N(4)	2 712(10)	3 284(15)	5 299(27)
N(5)	2 173(10)	2 577(17)	4 935(28)
N(6)	5 768(11)	1 602(17)	10 131(32)
N(7)	1 736(11)	879(18)	5 301(30)
N(8)	3 394(9)	3 428(15)	9 083(28)
N(9)	3 362(10)	2 927(17)	10 459(33)
N(10)	3 341(13)	2 452(22)	11 863(37)
C(1)	5 276(12)	2 135(20)	9 379(38)
C(2)	4 806(11)	4 736(18)	7 388(31)
C(3)	5 456(13)	5 429(21)	7 846(37)
C(4)	4 240(12)	5 252(19)	6 463(34)
C(5)	4 224(12)	6 415(20)	6 005(35)
C(6)	3 685(15)	6 871(25)	5 036(47)
C(7)	3 150(12)	6 142(20)	4 600(35)
C(8)	3 192(12)	5 031(19)	5 063(35)
C(9)	2 637(12)	4 235(20)	4 616(35)
C(10)	2 046(13)	4 615(21)	3 296(36)
C(11)	2 262(13)	1 550(20)	5 568(36)
C(12)	5 532(23)	296(40)	5 260(66)

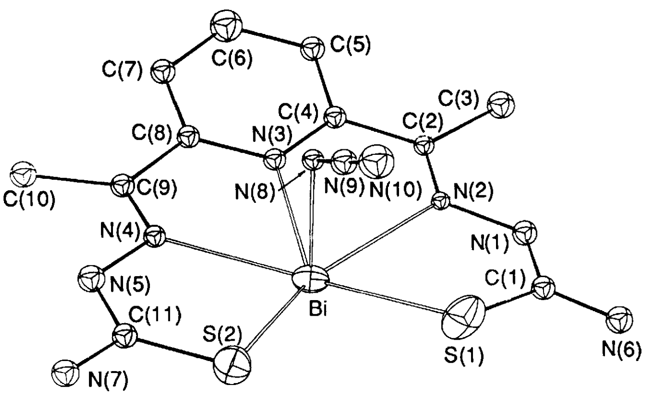
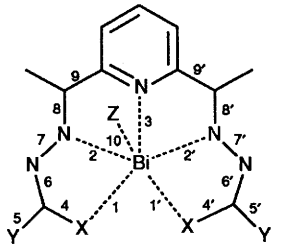


Figure 2. Perspective view of the [Bi(dapts)(N_3)] molecule

by 0.352(1) Å in the direction opposite to the apex [angles involving Bi and N(8): 74.5(6)—89.1(5)°]. The chelation is asymmetrical with bond distances Bi–N(3) 2.44(2) and Bi–N(4) 2.46(2) Å which agree with the values found in (**1**) and (**3**), and Bi–N(2) 2.58(2) Å significantly longer than the others, while the two Bi–S bonds 2.685(7) and 2.717(8) Å are strictly similar and in the range commonly found.[21] In each of the four chelated rings bismuth deviates from the least-squares plane by 0.827(2) [ring S(1),N(2)], 0.156(2) [ring N(2),N(3)], 0.273(2) [ring N(3),N(4)], and 0.312(2) Å [ring N(4),S(2)] respectively. The atoms of the ring formed by S(1),C(1),N(1),N(2) lie in a main plane bent with respect to those of the other chelated rings (these are approximately coplanar) forming dihedral angles in the range 13(1)—15(1)°. The Bi–N(8) bond 2.25(2) Å is very short and near to the sum of the covalent radii (2.21 Å), and considerably differs from the values 2.35(1)—2.90(1) Å previously cited. One example of a bismuth azide organometallic compound is $[(\mathrm{BiMe_2})_2\mathrm{N_3}]$[22] in which the azide group is bridging two adjacent $\mathrm{BiMe_2}$ groups in polymeric chains: the Bi–N distances are 2.484 Å and 2.499 Å, and angles at the doubly bonded nitrogen atom are Bi–N–N 117.1, Bi′–N–N 120.1, and Bi–N–Bi′ 122.8°. Also in the present case the Bi–N(8)–N(9) angle is 121(1)°. Bond distances and angles involving the ligand molecule are normal and in agreement with those found in (**1**) and (**3**); the $\mathrm{N_3}^-$ ion is linear within experimental errors [N(8)–N(9)–N(10) 178(3)°]. The molecules are packed by means of contacts formed by the bismuth atom in the direction opposite to the azide: Bi···N(10^{III}) (III $x, y, z-1$) 3.53(2) Å and by hydrogen bonds N(6)···N(5^{IV}) 3.15(3), N(6)–H(1)···N(5^{IV}) (IV $\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$) 165(3)°, N(7)···N(8^{V}) (V $\frac{1}{2}-x$, $y-\frac{1}{2}$, $\frac{3}{2}-z$) 2.98(3) Å, N(7)–H(4)···N(8^{V}) 154(4)°. The dimethyl sulphoxide molecule is disordered about a symmetry centre located on (0, $\frac{1}{2}$, 0); its O(1) oxygen is located 2.94(5) Å from bismuth on the opposite side of the $\mathrm{N_3}$ group.

Table 4. Comparative bond distances (Å) and angles (°) in complexes (**1**)—(**3**)



	[Bi(dapt)(OH)]·dmso·H_2O	[Bi(dapt)Cl]·dmso	[Bi(dapts)(N_3)]·0.5dmso
	X = O, Y = C_4H_3S, Z = OH	X = O, Y = C_4H_3S, Z = Cl	X = S, Y = NH_2, Z = N_3
1,1′	2.43(1), 2.41(1)	2.43(2), 2.48(2)	2.717(8), 2.685(7)
2,2′,3	2.49(1), 2.46(1), 2.44(1)	2.48(2), 2.47(2), 2.47(2)	2.58(2), 2.46(2), 2.44(2)
4,4′	1.24(2), 1.25(2)	1.25(3), 1.26(3)	1.80(3), 1.71(2)
5,5′	1.47(2), 1.49(3)	1.46(3), 1.50(3)	1.28(3), 1.36(3)
6,6′	1.33(2), 1.33(3)	1.34(3), 1.31(3)	1.36(3), 1.31(3)
7,7′	1.40(2), 1.38(2)	1.38(3), 1.34(2)	1.39(3), 1.41(3)
8,8′	1.29(2), 1.31(2)	1.26(3), 1.29(3)	1.24(3), 1.24(3)
9,9′	1.49(2), 1.45(2)	1.53(4), 1.49(3)	1.43(3), 1.51(3)
10	2.08(1)	2.472(7)	2.25(2)
1,1′	99.4(4)	97.6(5)	85.7(2)
1,2	64.1(4)	64.4(5)	69.9(4)
2,3	64.7(4)	65.6(6)	62.9(6)
2′,3′	65.9(4)	65.6(6)	66.2(6)
1′,2′	64.4(4)	65.1(6)	71.7(5)
Σ angles	358.5	358.3	356.4
1,10	80.9(4)	86.7(4)	84.2(5)
2,10	87.0(5)	83,8(4)	82.6(6)
3,10	87.1(4)	83.2(4)	74.6(6)
2′,10	85.4(5)	85.6(4)	77.3(7)
1′,10	85.9(5)	82.6(4)	89.1(5)

References

1 C. Pelizzi, G. Pelizzi, and G. Predieri, *J. Organomet. Chem.*, 1984, **9**, 263.
2 S. Ianelli, M. Nardelli, and C. Pelizzi, *Gazz. Chim. Ital.*, 1985, **115**, 375.
3 M. Ferrari Belicchi, G. Fava Gasparri, E. Leporati, C. Pelizzi, P. Tarasconi, and G. Tosi, *J. Chem. Soc., Dalton Trans.*, 1986, 2455.
4 C. Pelizzi, G. Pelizzi, and F. Vitali, *J. Chem. Soc., Dalton Trans.*, 1987, 177.
5 C. Lorenzini, C. Pelizzi, G. Pelizzi, and G. Predieri, *J. Chem. Soc., Dalton Trans.*, 1983, 2155.
6 A. Bonardi, C. Carini, C. Merlo, C. Pelizzi, G. Pelizzi, P. Tarasconi, F. Vitali, and F. Cavatorta, *J. Chem. Soc., Dalton Trans.*, 1990, 2771.
7 L. P. Battaglia, A. Bonamartini Corradi, G. Pelosi, P. Tarasconi, and C. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 1989, 671.
8 G. J. Palenik, D. Wester, U. Rychlewska, and R. C. Palenik, *Inorg. Chem.*, 1976, **15**, 1814.
9 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
10 G. M. Sheldrick, SHELX 76 program for crystal structure determination, Cambridge University, 1976.
11 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, 1965.
12 M. Nardelli, *Comput. Chem.*, 1983, **7**, 95.
13 N. S. Biradar and B. R. Havinale, *Inorg. Chim. Acta*, 1976, **17**, 157.
14 M. F. Iskander and S. Saddeck, *Inorg. Chim. Acta*, 1977, **22**, 141.
15 S. Padhye and G. B. Kauffmann, *Coord. Chem. Rev.*, 1985, **63**, 127.
16 W. F. Currier and J. H. Weber, *Inorg. Chem.*, 1967, **6**, 1539.
17 N. Bertazzi, G. Alonzo, L. P. Battaglia, A. Bonamartini Corradi, and G. Pelosi, *J. Chem. Soc., Dalton Trans.*, 1990, 2403.
18 F. C. March and G. Ferguson, *J. Chem. Soc., Dalton Trans.*, 1975, 1291.
19 F. Lazarini, *Acta Crystallogr., Sect. B*, 1979, **35**, 448.
20 F. Lazarini, *Cryst. Struct. Commun.*, 1979, **8**, 69.
21 L. P. Battaglia and A. Bonamartini Corradi, *J. Chem. Soc., Dalton Trans.*, 1986, 1513 and refs. therein.
22 J. Muller, U. Muller, A. Loss, J. Lorberth, H. Donath, and W. Massa, *Z. Naturforsch, Teil B*, 1985, **40**, 1320.

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