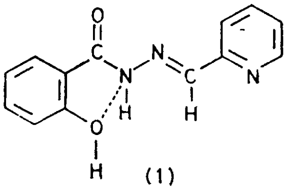
Crystal and Molecular Structure of (*N*-Picolinylidene-*N'*-salicyloylhydrazinato)(*N*-picolinylidene-*N'*-salicyloylhydrazine)copper(II) Perchlorate–Ethanol (1/1) †

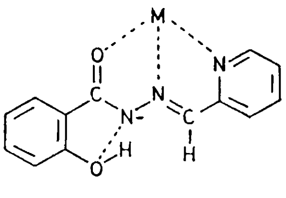
By **Paolo Domiano, Amos Musatti, Mario Nardelli,* Corrado Pelizzi,** and **Giovanni Predieri,** Istituto di Strutturistica Chimica e di Chimica Generale ed Inorganica, Università degli Studi, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., 43100 Parma, Italy

The crystal structure of the title complex has been determined from diffractometer data by three-dimensional Patterson, Fourier, and least-squares methods to R 0.049 for 3 072 independent reflections. Crystals are monoclinic, space group $P2_1/n$, with unit-cell dimensions a = 21.230(9), b = 11.493(5), c = 12.091(5) Å, β = 100.47(4)°, and Z = 4. The co-ordination around the metal is distorted square bipyramidal and involves both the deprotonated and the neutral organic ligands, which are chelated through the carbonyl oxygen [Cu–O(3) 2.062(3), Cu–O(1) 2.334(4) Å], a hydrazide nitrogen [Cu–N(5) 1.930(4), Cu–N(2) 2.043(4) Å], and the pyridine nitrogen [Cu–N(4) 2.081(3), Cu–N(1) 2.277(4) Å]. Packing is determined by a system of O–H ··· O hydrogen bonds involving the neutral ligand, the ethanol molecule, and the $[ClO_4]^-$ group.

PREVIOUSLY we have described the results of the crystal-structure analyses of *N*-picolinylidene-*N'*-salicyloylhydrazine [1] (Hsip) (1) and of its complexes bis(*N*-picolinylidene-*N'*-salicyloylhydrazinato)nickel(II) [2] and *catena*-μ-isothiocyanato-(*N*-picolinylidene-*N'*-salicyloylhydrazinato)copper(II),[3] which contain the ligand in the deprotonated form [see structure (2)]. The present work represents a further contribution to the knowledge of the behaviour of this chelating agent, giving the structure of a copper(II) complex where the ligand is present both in the neutral and in the anionic forms.



(1)



(2)

EXPERIMENTAL

Preparation of (*N*-picolinylidene-*N'*-salicyloylhydrazinato)(*N*-picolinylidene-*N'*-salicyloylhydrazine)copper(II) perchlorate–ethanol (1/1), $[Cu(sip)(Hsip)][ClO_4]\cdot EtOH$. The ligand Hsip was prepared as described in ref. 2. The salt $Cu[ClO_4]_2\cdot 6H_2O$ and Hsip (1 : 2 mol ratio) were heated under reflux in ethanol for *ca.* 30 min. By slow evaporation at room temperature, from the green solution, brown-green air-stable prismatic crystals were obtained (Found: C, 48.75; H, 2.85; Cu, 8.90; N, 12.1. $C_{28}H_{27}ClCuN_6O_9$ requires C, 48.7; H, 2.50; Cu, 9.20; N, 12.15%). The i.r. and electronic spectra of the complex were discussed previously.[4]

Crystal Data.—$C_{28}H_{27}ClCuN_6O_9$, M = 690.6, Monoclinic, a = 21.230(9), b = 11.493(5), c = 12.091(5) Å, β = 100.47(4)°, U = 2 901(2) Å^3, Z = 4, D_c = 1.62 g cm^{-3}, $F(000)$ = 1 352, Cu-K_α radiation, λ = 1.541 8 Å, μ(Cu-K_α) = 23.23 cm^{-1}, space group $P2_1/n$ (from systematic absences). Cell dimensions were determined from diffractometer measurements.

Intensity Data and Structure Analysis.—Intensities of 5 504 independent reflections were measured, using a Siemens automated diffractometer; 3 072 of these, having $I > 2\sigma(I)$, were considered observed and used in the analysis. The structure was solved by the heavy-atom method and refined by block-diagonal least squares (R 0.066). The contribution of the hydrogen atoms, located at this stage on a difference map and refined isotropically, improved the R value to 0.055. The final value of R (0.049) was achieved by considering the perchlorate oxygen atoms as statistically located in two positions, whose occupancy factors were 85 and 15% respectively. Atomic scattering factors were those of ref. 5 for non-hydrogen atoms and of ref. 6 for hydrogen atoms. The final positional parameters with their estimated standard deviations are given in Table 1. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22504 (15 pp.).‡ All calculations were performed on the CDC 6600 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (Bologna), with programs of Immirzi.[7]

RESULTS AND DISCUSSION

As shown in Figure 1, the two terdentate ligands sip and Hsip co-ordinate to copper through the oxygen and a nitrogen from the hydrazide group, and through the pyridine nitrogen in an elongated and distorted square-bipyramidal environment; sip is equatorial with Hsip orthogonal to it, the latter being involved in the two long apical interactions.

The Cu–O and Cu–N co-ordination distances (Table 2) are in agreement with the corresponding ones found in other bipyramidal copper(II) complexes,[8,9] the two apical ones being among the shortest distances observed in similar cases. Obviously this fact is related to the structural rigidity of the chelating ligand, whose approach to Cu is conditioned by the distance Cu–N(2). This distance is significantly longer than the corresponding Cu–N(5) contact formed by sip, suggesting that the negative charge, arising upon loss of the proton originally bound to N(6), is partially located on N(5). The analysis of the equatorial co-ordination plane shows

---

† [*N'*-(2-Pyridylmethylene)-*N''*-salicyloylhydrazido(1 –)-*NN'O*] [*N'*-(2-pyridylmethylene)-*N''*-salicyloylhydrazine-*NN'O*]-copper(II) perchlorate–ethanol (1/1).

‡ For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

small but significantly tetrahedral shifts: N(2) −0.020, N(4) 0.058, N(5) −0.049, O(3) 0.021, Cu 0.089 Å.

The two organic ligands sip and Hsip consist of three planar parts, the benzene ring, the pyridine ring, and the central chain, which are roughly coplanar: C(5)-↱C(6) 2.1(5), C(18)-↱C(19) 2.1(5), C(7)-↱C(8) 4.7(5), and C(20)-↱C(21) 1.3(5)°, as found previously.

Table 3 shows a comparison of the most significant bond distances in sip and Hsip in the studied complexes and in the free neutral molecule Hsip. These values indicate some delocalization in the central chain, with a tendency to localize the double bonds between

TABLE 1

Fractional atomic co-ordinates [× 10^4 for the non-hydrogen atoms and × 10^3 for hydrogen, O(5B), O(6B), O(7B), and O(8B) atoms] with estimated standard deviations in parentheses

	x/a	*y/b*	*z/c*
Cu	562(1)	1 444(1)	1 876(1)
Cl	−3 999(1)	−2 022(1)	−737(1)
O(1)	−525(1)	1 404(2)	1 978(2)
O(2)	−1 509(1)	−1 641(2)	1 010(3)
O(3)	476(1)	2 306(2)	363(2)
O(4)	973(1)	5 858(2)	806(2)
O(5)	−4 039(3)	−851(4)	−558(6)
O(6)	−4 544(2)	−2 561(3)	−1 392(4)
O(7)	−3 791(3)	−2 577(4)	300(4)
O(8)	−3 457(3)	−2 242(7)	−1 269(5)
O(9)	−2 290(2)	−3 247(3)	−53(4)
N(1)	1 431(1)	395(3)	1 598(3)
N(2)	209(1)	−174(3)	1 405(2)
N(3)	−432(1)	−393(3)	1 313(2)
N(4)	727(1)	1 240(3)	3 615(2)
N(5)	789(1)	3 009(3)	2 360(3)
N(6)	813(2)	3 836(3)	1 553(3)
C(1)	2 044(2)	680(4)	1 687(4)
C(2)	2 520(2)	−113(5)	1 567(4)
C(3)	2 349(2)	−1 254(4)	1 355(4)
C(4)	1 715(2)	−1 567(4)	1 263(3)
C(5)	1 277(2)	−724(3)	1 374(3)
C(6)	591(2)	−995(3)	1 256(3)
C(7)	−791(2)	490(3)	1 627(3)
C(8)	−1 487(2)	334(3)	1 555(3)
C(9)	−1 832(2)	−696(4)	1 257(3)
C(10)	−2 486(2)	−722(4)	1 233(4)
C(11)	−2 801(2)	262(5)	1 485(4)
C(12)	−2 474(2)	1 286(4)	1 758(4)
C(13)	−1 823(2)	1 314(4)	1 829(4)
C(14)	711(2)	301(4)	4 246(3)
C(15)	814(2)	339(4)	5 413(4)
C(16)	918(2)	1 395(5)	5 937(3)
C(17)	939(2)	2 370(4)	5 299(3)
C(18)	842(2)	2 282(4)	4 144(3)
C(19)	865(2)	3 262(3)	3 402(3)
C(20)	644(2)	3 373(3)	537(3)
C(21)	655(2)	4 175(3)	−413(3)
C(22)	496(2)	3 793(4)	−1 517(3)
C(23)	510(2)	4 520(4)	−2 411(3)
C(24)	686(2)	5 671(4)	−2 205(4)
C(25)	837(2)	6 089(3)	−1 140(4)
C(26)	822(2)	5 358(3)	−223(3)
C(27)	−2 375(3)	−4 334(6)	492(5)
C(28)	−2 526(3)	−5 303(6)	−304(6)
O(5B)	−437(2)	−121(3)	−16(3)
O(6B)	−458(2)	−233(4)	−42(4)
O(7B)	−355(2)	−280(3)	−51(3)
O(8B)	−384(1)	−135(2)	−157(2)
H(1)	216(2)	144(4)	177(4)
H(2)	298(2)	14(4)	166(4)
H(3)	266(2)	−177(5)	134(4)
H(4)	158(2)	−230(4)	110(3)
H(6)	43(2)	−170(4)	103(3)
H(10)	−268(2)	−139(4)	106(4)
H(11)	−326(2)	23(4)	154(4)
H(12)	−270(2)	191(4)	194(3)
H(13)	−159(2)	192(4)	215(3)
H(14)	57(2)	−45(4)	384(3)
H(15)	81(2)	−33(4)	583(4)
H(16)	104(2)	145(5)	672(4)
H(17)	102(2)	309(4)	559(3)
H(19)	96(2)	407(4)	370(4)
H(22)	30(2)	307(4)	−178(3)
H(23)	35(2)	425(4)	−316(4)
H(24)	68(2)	617(4)	−282(3)
H(25)	102(2)	691(4)	−97(4)
H(271)	−186(3)	−453(5)	110(4)
H(272)	−278(3)	−430(6)	93(5)
H(281)	−220(3)	−457(6)	−71(6)
H(282)	−288(3)	−478(6)	−88(5)
H(283)	−249(3)	−590(6)	26(5)
H(73)	−59(2)	−107(4)	108(3)
H(82)	−176(2)	−207(4)	76(4)
H(84)	97(2)	531(4)	132(4)
H(89)	−263(3)	−286(6)	−40(5)

TABLE 2

Selected interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Co-ordination polyhedron

Cu–N(2)	2.043(4)	Cu–O(3)	2.062(3)
Cu–O(1)	2.334(4)	Cu–N(4)	2.081(3)
Cu–N(1)	2.277(4)	Cu–N(5)	1.930(4)
N(2)–Cu–N(4)	99.6(1)	O(1)–Cu–N(4)	86.1(1)
N(2)–Cu–O(3)	102.8(1)	O(1)–Cu–O(3)	97.3(1)
N(5)–Cu–O(3)	78.2(1)	N(1)–Cu–N(2)	75.3(2)
N(5)–Cu–N(4)	79.0(2)	N(1)–Cu–N(5)	111.9(2)
O(1)–Cu–N(2)	71.5(1)	N(1)–Cu–N(4)	95.7(2)
O(1)–Cu–N(5)	101.3(1)	N(1)–Cu–O(3)	93.9(1)

(*b*) Organic ligands

C(5)–C(6)	1.471(6)	C(18)–C(19)	1.447(6)
C(6)–N(2)	1.279(5)	C(19)–N(5)	1.275(6)
N(2)–N(3)	1.369(4)	N(5)–N(6)	1.370(6)
N(3)–C(7)	1.364(5)	N(6)–C(20)	1.327(5)
C(7)–O(1)	1.232(5)	C(20)–O(3)	1.284(5)
C(7)–C(8)	1.476(7)	C(20)–C(21)	1.477(6)
C(9)–O(2)	1.347(6)	C(26)–O(4)	1.355(5)
C(py)–C(py) (av.)	1.376(7)	C(Ph)–C(Ph) (av.)	1.386(7)
C(py)–N (av.)	1.339(6)		
C(4)–C(5)–C(6)	121.3(5)	C(17)–C(18)–C(19)	123.8(5)
N(1)–C(5)–C(6)	115.0(4)	N(4)–C(18)–C(19)	114.7(4)
C(5)–C(6)–N(2)	118.2(4)	C(18)–C(19)–N(5)	115.0(4)
C(6)–N(2)–N(3)	120.0(4)	C(19)–N(5)–N(6)	122.1(4)
N(2)–N(3)–C(7)	116.0(3)	N(5)–N(6)–C(20)	110.0(4)
N(3)–C(7)–C(8)	119.8(4)	N(6)–C(20)–C(21)	115.5(4)
N(3)–C(7)–O(1)	119.1(4)	N(6)–C(20)–O(3)	123.7(4)
O(1)–C(7)–C(8)	121.1(4)	O(3)–C(20)–C(21)	120.8(4)
C(7)–C(8)–C(9)	126.0(5)	C(20)–C(21)–C(26)	120.9(4)
C(7)–C(8)–C(13)	115.8(4)	C(20)–C(21)–C(22)	121.0(4)
O(2)–C(9)–C(8)	118.3(4)	O(4)–C(26)–C(21)	124.6(4)
O(2)–C(9)–C(10)	121.8(5)	O(4)–C(26)–C(25)	116.0(4)
C(py)–N–C(py) (av.)	117.4(4)	N–C(py)–C(py) (av.)	122.9(5)
C(py)–C–C(py) (av.)	118.9(5)	C(Ph)–C–C(Ph) (av.)	120.0(5)

(*c*) Perchlorate ion

Cl–O(5)	1.369(5)	Cl–O(6)	1.421(5)
Cl–O(7)	1.405(5)	Cl–O(8)	1.440(8)
Cl–O(B) (av.)	1.39(4)		
O–Cl–O (av.)	109.2(5)	O(B)–Cl–O(B) (av.)	109(3)

(*d*) Hydrogen bonds

O(4)–H(84) · · · N(6)	2.539(5)	145(4)
N(3)–H(73) · · · O(2)	2.668(4)	127(4)
O(2)–H(82) · · · O(9)	2.653(5)	169(5)
O(9)–H(89) · · · O(8)	2.883(8)	171(6)
O(9)–H(89) · · · O(7B)	2.68(4)	141(6)

TABLE 3

Comparison of the most significant bond distances (Å) for sip and Hsip in various complexes and in free Hsip

Bond [a]	[Ni(sip)$_2$]	[Cu(sip)(NCS)]	[Cu(sip)(Hsip)][ClO$_4$]·EtOH sip	[Cu(sip)(Hsip)][ClO$_4$]·EtOH Hsip	Hsip [b]
C(7)–C(8)	1.489(6)	1.477(6)	1.477(6)	1.476(7)	1.493
C(7)–O(1)	1.257(5)	1.281(5)	1.284(5)	1.232(5)	1.230
C(7)–N(3)	1.353(5)	1.345(5)	1.327(5)	1.364(5)	1.359
N(3)–N(2)	1.363(5)	1.372(5)	1.370(6)	1.369(4)	1.375
N(2)–C(6)	1.280(6)	1.285(5)	1.275(6)	1.279(5)	1.271
C(6)–C(5)	1.462(4)	1.455(6)	1.447(6)	1.471(6)	1.475
C(5)–N(1)	1.363(5)	1.363(5)	1.359(6)	1.343(5)	1.344
N(1)–C(1)	1.311(6)	1.338(5)	1.326(6)	1.328(5)	1.333

[a] The labels of the atoms refer to the Hsip ligand in the present work. [b] Estimated standard deviations are in the range 0.005—0.010 Å.

C(7) and O(1), and N(2) and C(6). As expected, this tendency is more pronounced in the protonated form, when no negative charge is available, especially for the carbonyl group whose bond distance in Hsip corresponds well with that expected for a pure double bond (1.23 Å). The C(7)–C(8) and C(6)–C(5) bonds, which link the central chain to the peripheral rings, have similar lengths in Hsip, and appear too long to allow conjugation between the extreme aromatic rings through the central chain. Nevertheless, in the sip ions the C(6)–C(5) distances, involving the pyridine ring, are significantly shorter than the C(7)–C(8) distances involving the phenyl ring. Moreover, in the case of the sip ion, there are small but significant differences between the two C–N distances in the pyridine ring, that involving the carbon connected to the central chain being longer. These facts suggest that some π interaction between the central chain and the pyridine ring may be present in order to allow some localization of the negative charge also on the pyridine nitrogen. No relevant differences between co-ordinated and free Hsip are observed except for the change of conformation: in the metal complexes the nitrogen atom

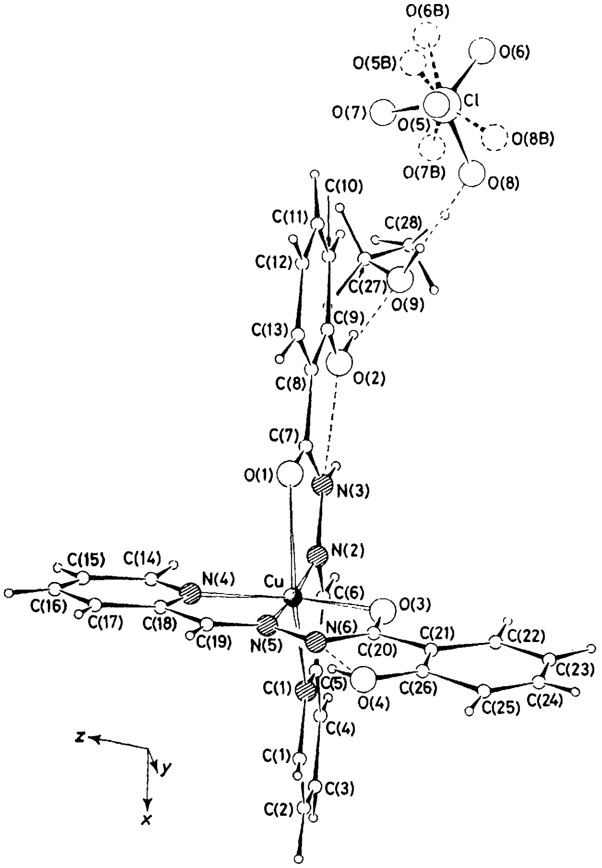


FIGURE 1 Clinographic projection of the structure

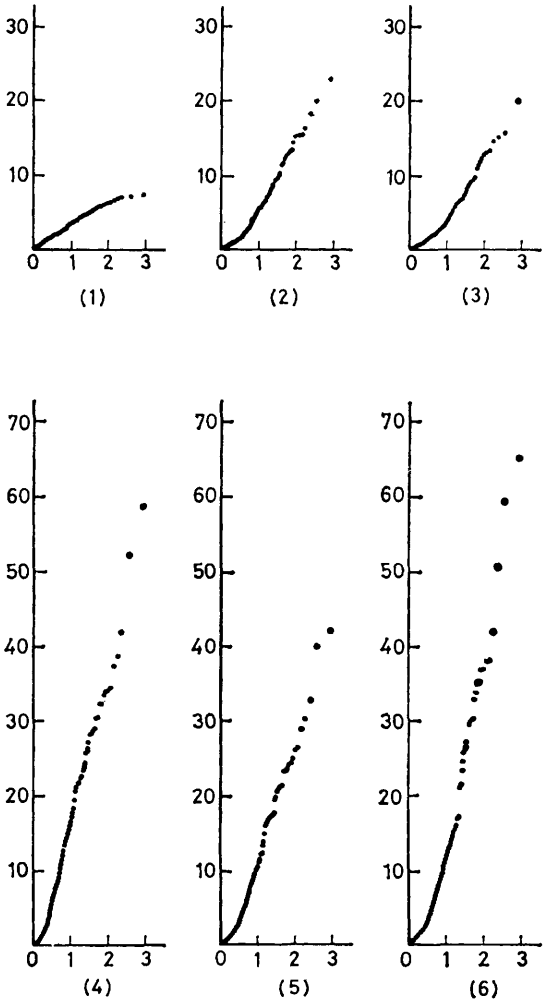


FIGURE 2 Half-normal probability plots for (1) sip in (A) with sip in (B), (2) sip in (A) with sip in (C), (3) sip in (B) with sip in (C), (4) sip and Hsip in (A), (5) Hsip in (A) with sip in (B), and (6) Hsip in (A) with sip in (C), where (A) = [Cu(sip)(Hsip)]-[ClO$_4$]·EtOH, (B) = [Ni(sip)$_2$], and (C) = [Cu(sip)(NCS)]

is *syn* with respect to the carbonyl group, enabling terdentate co-ordination to the metal, whereas it is *anti* in the free molecule. In the Hsip ligand of the present complex an intramolecular N–H · · · O hydrogen bond (2.67 Å) is present, as found in free Hsip, whereas in the sip ion a much stronger N · · · H–O interaction (2.54 Å) favoured by the presence of the negative charge on N(6) is observed.

TABLE 4

Parameters obtained from half-normal probability plots

	No. of distances	Maximum $(\Delta/\sigma)_{obs.}$	Gradient	Intercept	Correlation coefficient	No. of distances with $\Delta/\sigma > 3$	No. of bond distances with $\Delta/\sigma > 3$
(1) sip in (A) with sip in (B)	153	7.40	3.06(3)	0.33(3)	0.981	59	2
(2) sip in (A) with sip in (C)	153	23.08	7.60(12)	−1.58(12)	0.982	72	
(3) sip in (B) with sip in (C)	153	20.04	6.16(12)	−1.35(12)	0.975	58	1
(4) sip and Hsip in (A)	153	58.81	19.42(16)	−3.10(12)	0.995	106	2
(5) Hsip in (A) with sip in (B)	153	42.15	14.55(17)	−2.85(17)	0.989	95	1
(6) Hsip in (A) with sip in (C)	153	65.36	19.88(42)	−5.23(42)	0.968	99	2

(A) = $[Cu(sip)(Hsip)][ClO_4]\cdot EtOH$, (B) = $[Ni(sip)_2]$, and (C) = [Cu(sip)(NCS)]. In all cases the estimated standard deviations appear underestimated.

The perchlorate ion is disordered into two statistical positions, whose occupancy factors are 85 and 15%. Distances and angles in the first position agree fairly well with those found in other disordered perchlorates;[10,11] in the second position they cannot be considered as accurate, the occupancy factors being very small. Bond distances and angles in the ethanol molecule [C–C 1.47(1), C–O 1.440(8) Å] are quite as expected. The presence of this molecule seems justified by its acting as a hydrogen-bonding bridge between the $[ClO_4]^-$ ion and the Hsip ligand. In this respect it is of note that the $[ClO_4]^-$ ion is involved in hydrogen bonding in both disordered positions.

In Figure 2 the molecular geometries of the sip and Hsip ligands in the present work (A), in $[Ni(sip)_2]$ (B), and in [Cu(sip)(NCS)] (C) are compared, using half-normal probability plots [12] and considering the interatomic distances as suggested by De Camp [13] and by Albertsson and Schultheiss.[14] In this analysis all the possible contacts have been considered. From the data obtained from these plots, given in Table 4, it can be seen that there are no significant differences between the structural parameters of the co-ordinating sip and Hsip, if only bond distances are considered, except for a few cases involving the carbonylic CO bond and sometimes the adjacent CN bond. These differences, which have been discussed previously, seem influenced by the deprotonation and also by the interaction of the carbonylic oxygen with the metal. In contrast, there are several significant differences between interatomic non-bonding distances and this indicates that some distortion is present in the ligands.

[8/1047 *Received, 5th June,* 1978]

REFERENCES

[1] P. Domiano, A. Musatti, C. Pelizzi, and G. Predieri, *Cryst. Struct. Comm.*, 1974, **3**, 531.

[2] P. Domiano, A. Musatti, M. Nardelli, and C. Pelizzi, *J.C.S. Dalton*, 1975, 295.

[3] P. Domiano, A. Musatti, M. Nardelli, C. Pelizzi, and G. Predieri, *J.C.S. Dalton*, 1975, 2358.

[4] C. Pelizzi and G. Predieri, *Gazzetta*, 1975, **105**, 413.

[5] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

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

[7] A. Immirzi, *Ricerca Sci.*, 1967, **37**, 743.

[8] I. D. Brown, C. P. Weiss, and K. K. Wu, ' Bond Index to the Determination of Inorganic Crystal Structures (BIDICS),' Institute for Material Research, McMaster University, Hamilton, Ontario, 1969—1971.

[9] I. D. Brown and K. L. K. Ho, ' BIDICS,' 1972.

[10] A. Camerman, L. H. Jensen, and A. T. Balaban, *Acta Cryst.*, 1969, **B25**, 2623.

[11] B. Figgis, L. Wadley, and J. Graham, *Acta Cryst.*, 1972, **B28**, 187.

[12] S. C. Abrahams and E. T. Keve, *Acta Cryst.*, 1971, **A27**, 157.

[13] V. H. De Camp, *Acta Cryst.*, 1973, **A29**, 148.

[14] J. Albertsson and P. M. Schultheiss, *Acta Cryst.*, 1974, **A30**, 854.