Crystal Structure and Spectral Properties of Bis(6-amino-1,3-dimethyl-5-phenylazoniumuracil)tetrachlorocuprate(II)

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The crystal structure of $[C_{12}H_{14}N_5O_2]_2[CuCl_4]$ was determined by single-crystal X-ray diffractometry at room temperature. The space group is $P\bar{1}$ with $Z = 2$ and $a = 9.502(2)$, $b = 12.650(2)$, $c = 14.715(5)$ Å, $\alpha = 68.94(2)$, $\beta = 70.71(2)$, $\gamma = 79.01(2)°$, and $V = 1552.6(4)$ Å^3. A final R value of 0.069 was obtained. The structure consists of $[CuCl_4]^{2-}$ anions and protonated 6-amino-1,3-dimethyl-5-phenylazoniumuracil cations which are linked through N–H···Cl hydrogen bonds. The $[CuCl_4]^{2-}$ anion shows a flattened tetrahedral geometry with the two largest Cl–Cu–Cl angles 124.8 and 126.7°. Three of the Cu–Cl distances are in the range 2.22–2.23 Å, while one is 2.30 Å. Reflectance UV-VIS spectra contain a d–d band at $7.9 \cdot 10^3$ cm^{-1} and a charge transfer band at $19.1 \cdot 10^3$ cm^{-1}.

The halocuprate(II) anions adopt geometries ranging from square-planar through tetrahedral to trigonal bipyramidal. Compounds with large cations usually contain CuX_4^{2-} ions, which are "flattened" tetrahedra with nearly or exactly D_{2d} symmetry. The distortion from T_d symmetry (regular tetrahedron) has been correlated with the electronic absorption spectrum. In particular, the d–d transition maximum increases in energy as the geometry distorts from a regular tetrahedron towards a square plane.[1] Pellacani et al.[2] and Simonsen et al.[3] have established linear relationships between energy of the most intense d–d transition and the distortion from T_d symmetry, using quite different distortion parameters. The geometry of the anion is a compromise between intra- and intermolecular forces, and it has recently been proposed that strong hydrogen bonding favours a planar geometry.[4] Since the 6-amino-1,3-dimethyl-5-phenylazoniumuracil cation is a potential hydrogen bond donor, a crystal structure determination of the title compound was undertaken. A further interest in this compound derives from the potential antitumour activity of 5-arylazouracil derivatives and their complexes.[5,6]

Experimental

All chemicals used were of reagent grade and were used without further purification. 6-amino-1,3-dimethyl-5-phenylazouracil (DZH) was prepared as reported previously.[7] $[DZH_2]_2[CuCl_4]$ was obtained by adding a hot ethanolic solution (25 ml) of $CuCl_2 \cdot 2H_2O$ (0.33 g) to a boiling solution of DZH (1.0 g) in ethanol (25 ml) containing 2 ml 1

M HCl. Red crystals were formed after two days at room temperature. They were filtered off, washed with ethanol and dried with diethyl ether (yield 35 %). Carbon, hydrogen and nitrogen analyses were performed on a Perkin-Elmer 2040 microanalyser and copper was determined as CuO on a Mettler TG-50 thermobalance. Found: Cu 8.61; C 39.44; H 3.91; N 19.13. Calc. for $CuC_{24}H_{28}N_{10}O_4Cl_4$: Cu 8.76; C 38.70; H 3.86; N 19.30.

The reflectance spectrum of the solid compound was recorded using a Kontron-Uvikon 810 spectrophotometer with $BaSO_4$ as reference, and a Hitachi Perkin-Elmer 330 with an integrating sphere as detector using $MgSO_4$ as reference. In the range $5-40 \cdot 10^3$ cm^{-1}, absorption bands were observed at $23.0 \cdot 10^3$ and $30.3 \cdot 10^3$ cm^{-1} corresponding to transitions wihtin the organic ion, at $19.1 \cdot 10^3$ cm^{-1}, which probably is a charge transfer band, and at $7.9 \cdot 10^3$ cm^{-1}, which was assigned to d–d transition (vide infra).

A single crystal with the dimensions $0.32 \times 0.38 \times 0.28$ mm was used for the data collection on an Enraf Nonius CAD-4 diffractometer employing graphite-monochromated MoKα radiation ($\lambda = 0.7107$ Å). Laue symmetry $\bar{1}$ gives $P1$ and $P\bar{1}$ as possible choices for the space group ($Z = 2$). Cell dimensions were obtained by least-squares calculations of 50 θ-values determined as $\theta_{hkl} = (\omega_{hkl} - \omega_{hkl})/2$; $a = 9.502$ (2), $b = 12.650(2)$, $c = 14.715(5)$ Å, $\alpha = 68.94(2)$, $\beta = 70.71$ (2), $\gamma = 79.01(2)°$, $V = 1552.6(4)$ Å^3. The intensity of 5756 reflections in one half of the reflection sphere obeying $3 < \theta < 25°$ was measured with the $\omega-2\theta$ scan technique ($\Delta\omega = 0.85 + 0.5\tan\theta$). The scan interval was extended by 25 % at both ends for the background measurement. The

Table 1. Final positional and thermal parameters for the refined atoms. Estimated standard deviations in the last significant digit(s) are given in parentheses.

Atom	x/a	y/b	z/c	U_{iso} [a]/Å²
Cu	0.80141(10)	0.71548(7)	0.12974(6)	0.0412(4)
Cl1	0.97248(19)	0.84259(14)	0.04681(13)	0.0465(7)
Cl2	0.92604(24)	0.56544(14)	0.22494(15)	0.0580(9)
Cl3	0.73287(26)	0.71314(16)	0.00020(15)	0.0631(10)
Cl4	0.58212(23)	0.73580(18)	0.24261(17)	0.0685(10)
C1A	0.1735(11)	0.9694(6)	0.1601(6)	0.063(4)
C2A	0.2529(9)	0.9205(7)	0.3175(6)	0.053(3)
C3A	0.3476(12)	0.8836(8)	0.4646(7)	0.081(5)
C4A	0.2708(8)	0.7261(6)	0.4309(5)	0.049(3)
C5A	0.2135(7)	0.6922(5)	0.3685(4)	0.037(3)
C6A	0.1824(7)	0.7729(5)	0.2793(5)	0.038(3)
C7A	0.1791(8)	0.3914(5)	0.4839(5)	0.043(3)
C8A	0.1119(8)	0.3657(6)	0.4255(5)	0.045(3)
C9A	0.0874(10)	0.2543(7)	0.4494(7)	0.056(4)
C10A	0.1251(11)	0.1703(6)	0.5293(7)	0.067(4)
C11A	0.1898(13)	0.1999(8)	0.5840(8)	0.076(5)
C12A	0.2210(10)	0.3110(6)	0.5652(6)	0.059(3)
N1A	0.2055(6)	0.8829(4)	0.2562(4)	0.042(2)
N3A	0.2851(7)	0.8423(5)	0.4024(4)	0.049(3)
N5A	0.1876(6)	0.5868(4)	0.3854(4)	0.038(2)
N6A	0.1314(8)	0.7427(5)	0.2195(4)	0.047(3)
N7A	0.2094(9)	0.5057(7)	0.4623(6)	0.048(3)
O2A	0.2683(8)	1.0211(5)	0.2950(5)	0.082(3)
O4A	0.3016(7)	0.6617(4)	0.5073(4)	0.064(3)
C1B	0.9366(11)	0.2698(7)	0.2276(7)	0.072(4)
C2B	0.7923(9)	0.1503(5)	0.1995(6)	0.049(3)
C3B	0.6659(10)	0.0190(6)	0.1722(7)	0.069(4)
C4B	0.6807(8)	0.2159(6)	0.0613(5)	0.045(3)
C5B	0.7264(8)	0.3283(5)	0.0379(5)	0.046(3)
C6B	0.8094(8)	0.3465(5)	0.0929(6)	0.047(3)
C7B	0.5947(9)	0.5295(7)	−0.1644(5)	0.055(3)
C8B	0.6354(9)	0.6329(9)	−0.1791(6)	0.060(4)
C9B	0.5964(12)	0.7247(8)	−0.2519(8)	0.070(5)
C10B	0.5186(10)	0.7134(7)	−0.3120(6)	0.059(3)
C11B	0.4796(9)	0.6065(9)	−0.2942(6)	0.063(4)
C12B	0.5188(10)	0.5174(7)	−0.2234(7)	0.057(4)
N1B	0.8441(7)	0.2582(4)	0.1697(4)	0.048(2)
N3B	0.7136(6)	0.1345(4)	0.1431(4)	0.038(2)
N5B	0.6964(8)	0.4244(6)	−0.0333(5)	0.068(3)
N6B	0.8535(8)	0.4471(5)	0.0702(6)	0.081(4)
N7B	0.6248(8)	0.4171(6)	−0.0841(5)	0.066(3)
O2B	0.8190(7)	0.0757(4)	0.2723(4)	0.070(3)
O4B	0.6167(7)	0.1969(5)	0.0091(5)	0.073(3)
H6A1	0.123(13)	0.810(10)	0.115(8)	0.16(5)
H6A2	0.102(7)	0.688(5)	0.224(5)	0.03(2)
H7A	0.232(6)	0.514(5)	0.484(4)	−0.02(1)
H8A	0.095(6)	0.421(5)	0.370(4)	0.03(2)
H9A	0.022(8)	0.251(6)	0.434(5)	0.03(2)
H10A	0.099(8)	0.073(6)	0.543(5)	0.07(2)
H11A	0.203(9)	0.156(6)	0.620(6)	0.05(3)
H12A	0.303(7)	0.344(5)	0.601(4)	0.04(2)
H8B	0.690(11)	0.643(8)	−0.150(7)	0.09(3)
H9B	0.622(8)	0.776(6)	−0.268(5)	0.03(2)
H10B	0.430(14)	0.776(10)	−0.306(8)	0.14(5)
H11B	0.433(9)	0.567(6)	−0.331(5)	0.07(2)
H12B	0.494(7)	0.461(5)	−0.211(4)	0.02(2)

[a]For the non-hydrogen atoms, these values have been calculated from the average of the anisotropic temperature factors.

Table 2. Selected interatomic distances (Å) and angles (°), with estimated standard deviations in the last digit given in parentheses.

A. Coordination geometry of the tetrachlorocuprate(II)ion

Cu-Cl1	2.234(2)	Cl1-Cu-Cl2	102.86(8)	Cl2-Cu-Cl3	124.84(8)
Cu-Cl2	2.301(2)	Cl1-Cu-Cl3	99.74(8)	Cl2-Cu-Cl4	102.77(9)
Cu-Cl3	2.220(2)	Cl1-Cu-Cl4	126.70(8)	Cl3-Cu-Cl4	102.54(9)
Cu-Cl4	2.232(2)				

B. Geometry of the two 6-amino-1,3-dimethyl-5-phenylazoniumuracil ions

C1A-N1A	1.53(1)	C1A-N1A-C2A	118.7(5)	C1B-N1B	1.47(1)	C1B-N1B-C2B	116.1(6)
N1A-C2A	1.38(1)	C1A-N1A-C6A	118.8(5)	N1B-C2B	1.41(1)	C1B-N1B-C6B	121.9(6)
C2A-O2A	1.22(1)	N1A-C2A-O2A	120.2(7)	C2B-O2B	1.21(1)	N1B-C2B-O2B	119.7(7)
C2A-N3A	1.37(1)	N1A-C6A-N6A	119.7(6)	C2B-N3B	1.37(1)	N1B-C6B-N6B	120.5(7)
N3A-C3A	1.51(1)	N1A-C2A-N3A	118.7(6)	N3B-C3B	1.48(1)	N1B-C2B-N3B	117.6(6)
N3A-C4A	1.40(1)	N1A-C6A-C5A	118.6(6)	N3B-C4B	1.36(1)	N1B-C6B-C5B	118.9(6)
C4A-O4A	1.22(1)	O2A-C2A-N3A	121.1(7)	C4B-O4B	1.23(1)	O2B-C2B-N3B	122.7(6)
C4A-C5A	1.42(1)	C2A-N3A-C3A	118.0(6)	C4B-C5B	1.45(1)	C2B-N3B-C3B	117.1(6)
C5A-C6A	1.43(1)	C2A-N3A-C4A	123.4(6)	C5B-C6B	1.40(1)	C2B-N3B-C4B	124.5(5)
C6A-N6A	1.32(1)	C3A-N3A-C4A	118.6(6)	C6B-N6B	1.31(1)	C3B-N3B-C4B	118.3(6)
C6A-N1A	1.35(1)	N3A-C4A-O4A	119.7(7)	C6B-N1B	1.35(1)	N3B-C4B-O4B	122.7(6)
C5A-N5A	1.32(1)	N3A-C4A-C5A	115.9(6)	C5B-N5B	1.34(1)	N3B-C4B-C5B	116.0(6)
N5A-N7A	1.27(1)	O4A-C4A-C5A	124.3(7)	N5B-N7B	1.20(1)	O4B-C4B-C5B	121.3(6)
N7A-C7A	1.43(1)	C4A-C5A-N5A	124.6(6)	N7B-C7B	1.54(1)	C4B-C5B-N5B	127.4(7)
C7A-C8A	1.38(1)	C4A-C5A-C6A	120.8(6)	C7B-C8B	1.36(1)	C4B-C5B-C6B	120.6(6)
C8A-C9A	1.37(1)	C6A-C5A-N5A	114.6(5)	C8B-C9B	1.36(1)	C6B-C5B-N5B	112.0(6)
C9A-C10A	1.37(1)	C5A-C6A-N6A	121.7(6)	C9B-C10B	1.38(1)	C5B-C6B-N6B	120.6(7)
C10A-C11A	1.34(1)	C5A-N5A-N7A	121.8(6)	C10B-C11B	1.38(1)	C5B-N5B-N7B	116.8(7)
C11A-C12A	1.40(1)	N5A-N7A-C7A	123.1(7)	C11B-C12B	1.32(1)	N5B-N7B-C7B	114.4(7)
C12A-C7A	1.38(1)	N7A-C7A-C12A	116.2(6)	C12B-C7B	1.36(1)	N7B-C7B-C12B	112.9(7)
		N7A-C7A-C8A	120.5(6)			N7B-C7B-C8B	126.5(7)
		C7A-C8A-C9A	117.7(7)			C7B-C8B-C9B	119.2(8)
		C8A-C9A-C10A	122.2(8)			C8B-C9B-C10B	120.7(9)
		C9A-C10A-C11A	117.8(8)			C9B-C10B-C11B	118.0(8)
		C10A-C11A-C12A	124.5(9)			C10B-C11B-C12B	120.8(8)
		C11A-C12A-C7A	114.5(8)			C11B-C12B-C7B	120.7(8)

C. Possible hydrogen bonds

Cl1-N6A	3.136(7)
Cl2-N6A	3.206(7)
Cl2-N6B	3.432(8)
Cl3-N6B	3.243(6)

ratio $\sigma(I)/(I)$ required in a scan was 0.028, and the maximum recording time 180 s. Three standard reflections were recorded at regular intervals.

I and $\sigma(I)$ were corrected for Lorentz, polarization and absorption effects, the latter by numerical integration ($\mu = 10.98$ cm^{-1}, transmission factors 0.7137–0.7996). Only the 4040 reflections with $I > 3\sigma(I)$ were considered significantly different from the background and were used in the calculations. The structure was solved by direct[8] and difference Fourier methods. For molecule A (Table 1) all but the methyl hydrogens were found, while for molecule B only five phenyl hydrogens could be located. The structure was refined in $P\bar{1}$ by full-matrix least-squares minimizing $\Sigma w(|F_o| - |F_c|)^2$ with weights $w^{-1} = \sigma_c^2(|F_o|) + (0.015|F_o|)^2$. In the final refinement anisotropic temperature factors were applied to all non-hydrogen atoms. The total number

of parameters refined was 441. Scattering factors with corrections for anomalous dispersion were taken from Ref. 9. The final agreement indices $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w^{-1/2} = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2$ were 0.069 and 0.094, respectively.

A difference Fourier after the refinement showed two residual peaks (1.8 eÅ^{-3}) near the azo bridge of molecule B, which could not be interpreted as due to a conformational disorder of the DZH molecule. They are probably the result of slight solid solubility of some of the reagents from the synthesis. These peaks were not included in the structural model.

Computer programs compiled and amended by Lundgren[10] were used. Final positional and thermal parameters are given in Table 1 and selected distances and angles in Table 2.
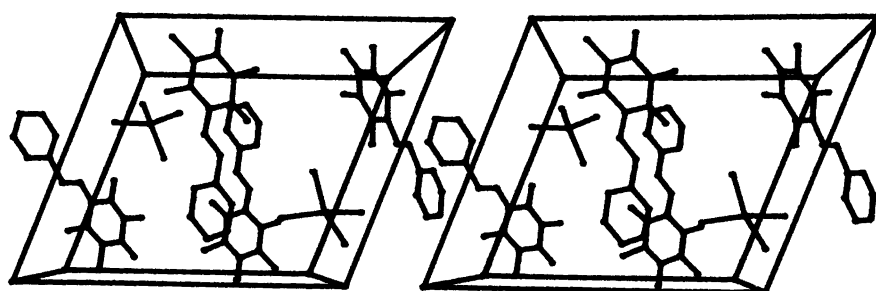
Fig. 1. A stereoscopic view of the packing units.

Description and discussion of the structure

The compound contains two crystallographically independent cations, DZH$_2^+$, and one anion, CuCl$_4^{2-}$, packed as shown in Fig. 1. The three-dimensional structure is further stabilized by N−H···Cl hydrogen bonding between the cations and anions (Table 2C). The numbering scheme of the cations is shown in Fig. 2. The azo nitrogen atom N7 is protonated and an intramolecular hydrogen bond, N7−H7···O4, is formed (d_{N-O} = 2.661(9) Å). The agreement between bond distances and angles in the two cations (Table 2B) as well as with relevant bond distances and angles in [DZH$_2$]$_2$[AuBr$_2$]Br · H$_2$O is good.[11]
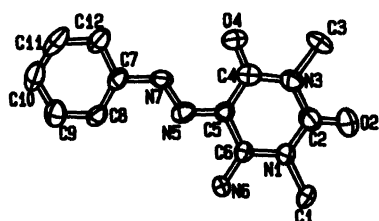

Fig. 2. The organic cation A viewed perpendicular to the LS-plane through the non-H atoms. The numbering scheme is the same for cation B.
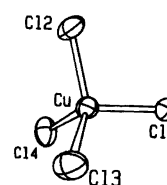

Fig. 3. The coordination geometry of the tetrachlorocuprate(II) ion.

As expected, the geometry of the ion CuCl$_4^{2-}$ is a "flattened" tetrahedron (Fig. 3; Table 2A). Three of the four Cu−Cl distances are close to 2.23 Å, while the fourth is significantly longer, viz. 2.30 Å. A possible explanation for this may be that Cl2 accepts two hydrogen bonds, while Cl1 and Cl3 accept only one each (Table 2C). Furthermore, these two latter hydrogen bonds should be weak since they have no measurable effect on the Cu−Cl distance. The Cl−Cu−Cl bond angles vary within the range 99.7 to 126.7°, showing a geometric intermediate between square-planar and tetrahedral; the symmetry is very approximately D_{2d}, especially taking in account the occurrence of one long Cu−Cl bond. The average of the two largest angles has been used to describe the distortion from tetrahedral geometry.[3] The value obtained in this structure, 125.8°, is among the smallest observed so far (Table 3). As seen in

Table 3. Geometrical parameters and optical bands for CuCl$_4^{2-}$ complexes in crystals.

Compound[a]	d−d band maximum/cm^{-1}·10^3	2θ/°	Hydrogen bonding	Reference
[DZH$_2$]$_2$[CuCl$_4$]	7.9	125.8	Yes	This paper
Cs$_2$[CuCl$_4$]	9.05	129.2	No	13, 14
[N(CH$_3$)$_4$]$_2$[CuCl$_4$]	9.0	129.4	No	15, 16
[TMBA]$_2$[CuCl$_4$]	9.0	130.	No	17
[C$_6$H$_5$CH$_2$N(CH$_3$)$_3$][CuCl$_4$]	9.25	132.5	No	18, 19
[(C$_2$H$_5$)$_3$NH]$_2$[CuCl$_4$]	9.4	135.	Yes	17, 20
[C$_5$H$_9$NH(CH$_3$)S]$_2$[CuCl$_4$]	9.8	135.05	Yes	21
[(CH$_3$)$_2$NH$_2$]$_3$[CuCl$_4$]	9.52	135.8	Yes	3, 22
[d-MAMPH]$_2$[CuCl$_4$]	10.20	138.3	Yes	3
[NPHPAZH$_2$][CuCl$_4$]	10.75	142.0	Yes	2
[C$_{13}$H$_{19}$N$_2$OS]$_2$[CuCl$_4$]	10.81	143.5	Yes	2, 23
[ClNH$_2$][CuCl$_4$]·3H$_2$O	11.1	146.	Yes	12
[C$_6$H$_5$CH$_2$N(CH$_3$)H$_2$]$_2$[CuCl$_4$]	16.1	180.	Yes	24

[a]TMBA = trimethylbutylammonium, d-MAMPH = (+)-N,N-dimethylphenethylammonium, NPHPAZH$_2$ = N-phenylpiperazinium, ClNH$_2$ = cinchonium.

Table 3, it is even smaller than the value observed in compounds with no hydrogen bonds, in conflict with the statement that hydrogen bonds to Cl favour a "planar" configuration.[4] Hoffmann *et al.*[12] have calculated the d orbital energies for a D_{2d} distorted $CuCl_4^{2-}$ tetrahedron with $d_{Cu-Cl} = 2.25$ Å, as a function of $\theta°$ ($2\theta° = \angle$ Cl–Cu–Cl) using the angular overlap model. The ground state is d_{xy}. The calculated $d-d$ band positions are $d_{xz,yz} \leftrightarrow d_{xy} = 4900$ cm^{-1} and $d_{xy} \leftrightarrow d_z^2 = 8300$ cm^{-1} (the $d_{xy} \leftrightarrow d_{x^2-y^2}$ transition is symmetry forbidden). The experimentally observed $d-d$ band position, $7.9 \pm 0.2 \cdot 10^3$ cm^{-1}, is fairly reasonable taking into account the fact that deviation from D_{2d} symmetry of the complex leads to a splitting (broadening) of the band.

References

1. Smith, D. W. *Coord. Chem. Rev. 21* (1976) 93 and references therein.
2. Battaglia, L. P., Bonamartini, A., Marcotrigiano, G., Menabue, L. and Pellicani, G. C. *Inorg. Chem. 18* (1979) 148.
3. Harlow, R. L., Wells, W. J., Watt, G. W. and Simonsen, S. H. *Inorg. Chem. 14* (1975) 1768.
4. Place, H. and Willet, R. D. *Acta Crystallogr., Sect. C43* (1987) 1050.
5. Hibino, S. *Cancer Chemotheraphy Reports 13* (1961) 41.
6. Ruiz-Sanchez, J. *Thesis,* UNED MADRID, Madrid 1988.
7. Ruiz-Sanchez, J., Colacio-Rodriguez, E., Salas-Peregrin, J. M. and Romero-Molina, M. A. *J. Anal. Appl. Pyrol. 9* (1986) 159.
8. Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, J. P., Declercq, J.-P. and Woolfson, M. M. *MULTAN: A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data,* University of York, England and Louvain, Belgium 1980.
9. *International Tables for X-Ray Crystallography,* Kynoch Press, Birmingham 1974, Vol. 4.
10. Lundgren, J. O. *Crystallographic Computer Programs, Report No. UUIC-B13-4-05,* University of Uppsala, Uppsala, Sweden 1982.
11. Ruiz, J. and Colacio, E. *To be published.*
12. Dyrek, K., Goslar, J., Hodorowicz, S. A., Hoffmann, S. K., Oleksyn, B. J. and Weselucha-Birczguska, A. *Inorg. Chem. 26* (1987) 1481.
13. McGinnety, A. J. *J. Am. Chem. Soc. 94* (1972) 8406.
14. Ferguson, J. *J. Chem. Phys. 40* (1964) 3406.
15. Willet, R. D., Liles, O. L. and Michelson, C. *Inorg. Chem. 6* (1967) 1885.
16. Clay, R., Murray-Rust, J. and Murray-Rust, P. *Acta Crystallogr., Sect. B31* (1975) 289.
17. Lamotte-Brasseur, J. *Acta Crystallogr., Sect. A30* (1974) 487.
18. Furlani, C., Cervona, E., Calzona, F. and Baldanza, B. *Theor. Chim. Acta 7* (1967) 375.
19. Bonamico, M., Dessy, G. and Viciago, A. *Theor. Chim. Acta 7* (1967) 367.
20. Lamotte-Brasseur, J., Dupont, L. and Dideberg, O. *Acta Crystallogr., Sect. B29* (1973) 241.
21. Brianso, M. C., Brianso, J. L., Gaete, W. and Ros, J. *Inorg. Chim. Acta 49* (1981) 263.
22. Willet, R. D. and Larsen, M. L. *Inorg. Chim. Acta 5* (1971) 175.
23. Bonamartini, A., Nardelli, M., Palmieri, C. and Pellizi, C. *Acta Crystallogr., Sect. B27* (1971) 1775.
24. Harlow, R. L., Wells, W. J., Watt, G. W. and Simonsen, S. W. *Inorg. Chem. 13* (1974) 2106.