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Synthesis and photolysis of a new series of Cu(I) complexes with tri-*o*-tolylphosphine and heterocyclic thiones as ligands. The crystal structure of (thiazolidine-2-thione)(tri-*o*-tolylphosphine)-copper(I)bromide

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Abstract

Reactions of $[Cu(totp)Br]_4$ (totp = tri-*o*-tolyl-phosphine) with heterocyclic thiones (L) (L = pyridine-2-thione (py2SH), pyrimidine-2-thione (pymtH), 1.3-thiazolidine-2-thione (tzdtH), 1-methyl-1,3-imidazoline-2-thione (meimtH), benz-1,3-imidazoline-2-thione (bzimtH$_2$) and quinoline-2-thione (qntH) afford mononuclear complexes of the general formula [Cu(totp)(L)Br]. The complexes have been characterized by elemental analyses and their IR, UV–Vis and ^{1}H NMR spectroscopic data. The photolysis in chloroform solutions of these complexes has also been investigated. A single-crystal X-ray diffraction study was carried out on the tzdtH complex [Cu(totp)(tzdtH)Br]. The pale yellow compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.4672(7)$, $b = 10.9818(8)$, $c = 14.293(1)$ Å, $\alpha = 93.059(2)$, $\beta = 67.912(2)$, $\gamma = 118.208(2)°$, $D_{calc} = 1.570$ Mg m^{-3}, $V = 1199.23(9)$ Å^3 and $Z = 2$. The complex exhibits an approximate trigonal planar CuSPBr core with Cu–S 2.290(1), Cu–P 2.256(1) and Cu–Br 2.413(0) Å. The actual structural type appears to depend upon the identity of the phosphine ligand which has a decreased flexibility because of the steric demands of the *ortho* positioned methyl groups.

Introduction

There is much current interest in the coordination chemistry of copper with sulfur-containing ligands due to the biological importance of copper–sulfur interactions in Cu^{I}/Cu^{II} redox systems [1]. During our previous studies in this area we have prepared and structurally characterized a series of mixed Cu(I) complexes containing phosphines and heterocyclic thiones as ligands. Using triphenyl-, tri-*m*-tolyl- or tri-*p*-tolyl-phosphine, two closely related basic structures, mononuclear or binuclear with tetrahedral coordination environment around the copper atom, have been realized, whereby two types of binuclear complexes with sulfur or halogen atoms as bridging ligands are observed [2–6].

Since the factors causing variations on copper(I) geometry may have, apart from the electronic, an essential steric basis, we were particularly interested in seeing the stabilizing influence of bulky π-acceptor ligands and the type of interaction which contributes to the stability of the geometry being preferred. On the basis of the observed characteristics for the complexes investigated, it may be concluded that the size of the thione ligands is reflected only in small differences within the coordination sphere. However, there is no appreciable difference in bulkiness/steric hindrance between triphenyl-, tri-*m*-tolyl- and tri-*p*-tolylphosphine, so that the contribution from the phosphine ligand has not yet been clarified. It was therefore of interest to include the more bulky tri-*o*-tolyl-phosphine in our investigations.

The present paper deals with the reaction of $[Cu(totp)Br]_4$ with several heterocyclic thiones (L), from which mononuclear copper(I) complexes [Cu(totp)(L)Br] with trigonal planar coordination have been isolated. As this type of mixed Cu(I) complex is uniquely exemplified by [Cu(PPh$_3$)-

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(pptu)Cl] (pptu = 1-phenyl-3-(2-pyridyl)-2-thiourea) [7], we have carried out an X-ray structure determination of [Cu(totp)(tzdtH)Br].

Experimental

Materials and instruments

Copper bromide and tri-*o*-tolylphosphine (Merck) were used as obtained, while the thiones (Merck or Aldrich) were recrystallized from hot ethanol prior to their use. All solvents used were of reagent grade.

IR, electronic and NMR spectra, conductivities, magnetic susceptibility measurements and elemental analyses of carbon, nitrogen and hydrogen were performed as described previously [2].

The photolyses and quantum yields measurements were carried out in 1 cm quartz cells using a high pressure HBO 200W/4 Osram lamp; a 2 cm water filter and a monochromator manufactured by Applied Photophysics were applied. All the photochemical work was carried out in the dark.

Preparation of the complexes

$[Cu(totp)Br]_4$ was prepared by heating equimolar quantities of CuBr and totp at 50–70 °C in acetonitrile, for about 30 min [2].

The complexes of the formula [Cu(totp)(L)Br], were prepared according to the following general procedure: a solution of 0.4 mmol of the appropriate thione in 20 ml of methanol was added to a solution of 0.1 mmol of $[Cu(totp)Br]_4$ and an excess of totp in 20 ml acetonitrile and the resulting solution was moderately heated for 30 min. It was then allowed to cool and the microcrystalline product thus formed was collected by filtration. The compounds were identified by elemental analyses and by their IR, UV–Vis and NMR spectra. Single crystals suitable for X-ray diffraction studies were obtained by slow evaporation of [Cu(totp)(tzdtH)Br] in acetonitrile.

X-ray analysis

Complete crystal data and parameters for data collection are reported in Table 1. The space group was determined by preliminary Weisenberg and precession photographs. Unit cell dimensions were derived from a least-squares refinement of the setting angles of 30 automatically centered reflections in the range of $11 < 2\theta < 23°$ on a Syntex $P2_1$ diffractometer upgraded by CRYSTAL LOGIC with Nb-filtered Mo Kα radiation. Three standard reflections measured every 97 reflections showed <3.0% intensity fluctuation. Lp and absorption correction were applied. Scattering factors were taken from the International Tables for X-ray Crystallography [8]. The structure was solved by direct methods and refined by full-matrix least-squares, in which $\Sigma w\Delta^2$ was minimized using SHELX76 [9]. The hydrogen atoms of the methyl groups were calculated as riding on carbon atoms at 0.96 A, the rest were located from a difference Fourier map. The non-H atoms were refined anisotropically and the H atoms isotropically.

TABLE 1. Summary of crystal and intensity collection data

Formula	$CuP(C_7H_7)_3S_2NC_3H_5Br$
Formula weight	567.03
a (Å)	9.4672(7)
b (Å)	10.9818(8)
c (Å)	14.293(1)
α (°)	93.059(2)
β (°)	67.912(2)
γ (°)	118.208(2)
V (Å^3)	1199.23(9)
Z	2
D_{calc} (Mg m^{-3})	1.570
D_{meas} (Mg m^{-3})	1.57
Space group	$P\bar{1}$
Radiation	Mo Kα ($\lambda = 0.71069$)
μ (cm^{-1})	27.87
Scan speed (°/min)	4.5
Scan range	1.9 plus α_1–α_2
2θ limit (°)	52.0
Data collected	4879
Data unique	4676
Data used	3994
$F_o >$	$4.0\sigma(F_o)$
R_{int}	0.0209
Range of hkl	$-11 \rightarrow 10$, $-11 \rightarrow 11$, $-16 \rightarrow 0$
$F(000)$	576
No. refined parameters	357
$\lvert\Delta/\sigma\rvert_{max}$	0.213
$(\Delta p)_{max}$ (e Å^{-3})	0.545
$(\Delta p)_{min}$ (e Å^{-3})	−0.676
S[a]	0.77
R (obs.)[b]	0.0294
R (all data)[b]	0.0369
R_w (obs.)[c]	0.0302
R_w (all data)[c]	0.0353

[a] $S = [\Sigma w(\Delta F)^2/(N-P)]^{1/2}$, N = no. of observed reflections, P = no. of parameters. [b] $R = \Sigma|\Delta F|/\Sigma|F_o|$. [c] $R_w = [\Sigma w(\Delta F)^2/\Sigma_w|F_o|^2]^{1/2}$.

The fractional coordinates of the atoms are listed in Table 2. See also 'Supplementary material'.

Results and discussion

All the prepared complexes are microcrystalline solids soluble in chloroform, acetonitrile, ethanol, methanol and acetone. The elemental analyses confirm their stoichiometry and their physical properties are in accordance with the proposed structures; they are reported in Table 3. Room temperature magnetic

TABLE 2. Positional parameters ($\times 10^4$) of the non-H atoms with e.s.d.s in parentheses

Atom	x	y	z
Br	4459.3(4)	2800.6(4)	−232.1(2)
Cu	1396.7(5)	1352.2(5)	824.7(3)
P	690.8(9)	721.6(7)	2483.1(5)
S(1)	−413(1)	1460.7(9)	168.6(6)
C(1)	635(4)	3062(3)	−531(2)
S(2)	−479(1)	3591(1)	−983.5(8)
C(2)	1422(5)	5270(4)	−1605(3)
C(3)	2886(5)	5356(4)	−1360(3)
N	2255(3)	4033(3)	−777(2)
C(11)	−305(3)	1656(3)	3361(2)
C(12)	−1733(4)	949(3)	4279(2)
C(13)	−2478(4)	1637(4)	4953(2)
C(14)	−1796(5)	3049(4)	4716(3)
C(15)	−396(4)	3757(3)	3820(3)
C(16)	382(4)	3100(3)	3122(2)
C(17)	1945(5)	3958(3)	2144(3)
C(21)	−787(4)	−1120(3)	3084(2)
C(22)	−294(4)	−1768(3)	3627(2)
C(23)	−1337(5)	−3158(3)	4054(2)
C(24)	−2888(5)	−3929(3)	3939(3)
C(25)	−3412(4)	−3307(3)	3429(3)
C(26)	−2383(4)	−1900(3)	2991(3)
C(27)	−3036(4)	−1267(4)	2458(3)
C(31)	2605(3)	1146(3)	2757(2)
C(32)	2880(4)	1876(3)	3556(2)
C(33)	4298(4)	2173(3)	3778(2)
C(34)	5486(4)	1776(4)	3190(3)
C(35)	5237(4)	1062(4)	2400(3)
C(36)	3795(4)	704(3)	2172(2)
C(37)	3529(5)	−195(4)	1356(2)

measurements on several species confirm that the central metal ion is diamagnetic Cu(I).

Spectroscopy

Vibrational spectra of the complexes investigated, registered in the range 4000–200 cm^{-1}, are in agreement with subsequent discussed X-ray diffraction data with respect to the monodentate sulfur donating character of the thione ligands. The major changes are observed for the thioamide I (upward shifts of 15–25 cm^{-1}) and thioamide III (downward shifts of 10–30 cm^{-1}) bands, while the vibrational absorptions of the phosphine aromatic rings are practically unchanged with respect to those of the free phosphine ligand. These values are in agreement with those reported for other metal–thione complexes [10–12]. In this context it is also useful to compare the present results with data available for the tzdt ligand and analogous copper thiazolidine complexes. Selected absorptions of coordinated tzdtH, [Cu(tptp)(tzdtH)Br]$_2$, [Cu(totp)(tzdtH)Br] and [Cu(PPh$_3$)$_2$(tzdtH)$_2$]NO$_3$ are given in Table 4. The IR spectra of the trigonal, tetrahedral and dimeric complex are almost similar, being mainly characterized by vibrational absorptions of coordinated tzdtH, which are scarcely influenced by coordination to copper.

The UV–Vis spectra of the complexes in chloroform solutions are dominated by one main broad band in the region 266–305 nm with two or three peaks accompanied by another one at 370–380 nm in the case of conjugated heterocyclic thiones. The first band is ascribed from the coexistence of intraligand transitions of the phosphine ligand, since the spectrum of the free phosphine consists of two bands at 249 and 279 nm respectively having log ϵ values (*c.* 3.456 and 4.221) smaller than those observed in the complexes (about 4.500). The intraligand transitions of thione ligands which are in the region of 280–305 nm in the free ligands have log ϵ values (*c.* 3.994–4.633), also smaller than those found in the complexes.

Photolysis

Room temperature irradiation of the complexes in chloroform at $\lambda_{exit} = 300$ nm causes the decomposition of the complexes within minutes, without evolution of new bands. In accordance to what we have observed previously in analogous mixed ligands complexes there is no difference on the decomposition

TABLE 3. Some physical properties and analytical data of the complexes

Complex	$\Phi_i 300^*$	Colour	Melting point (°C)	Elemental analysis: found (calc.) (%)		
				C	H	N
[Cu(totp)(py2SH)Br] (**1**)	0.169	bright yellow	125	55.84 (55.82)	4.75 (4.65)	2.67 (2.50)
[Cu(totp)(pymtH)Br] (**2**)	0.120	red	122	54.32 (53.57)	4.34 (4.46)	4.92 (5.00)
[Cu(totp)(tztdH)Br] (**3**)	0.030	pale yellow	134	50.22 (50.79)	4.77 (4.59)	2.62 (2.47)
[Cu(totp)(meimtH)Br] (**4**)	0.063	white	112	54.22 (53.38)	4.46 (4.80)	4.75 (4.98)
[Cu(totp)(bzimtH$_2$)Br] (**5**)	0.236	white	143	56.19 (56.38)	4.20 (4.19)	4.94 (4.70)
[Cu(totp)(qntH)Br] (**6**)	0.025	red	146	58.92 (59.11)	4.86 (4.60)	2.16 (2.30)

$\Phi_i 300^*$ = quantum yields of *i* complex at 300 nm.

TABLE 4. Selected absorption bands of tzdtH, [Cu(tptp)(tzdtH)Br]$_2$ (A), [Cu(totp)(tzdtH)Br] (B) and [Cu(PPh$_3$)$_2$(tzdtH)$_2$NO$_3$] (C)

tzdtH	A	B	C	Assignment
3160m	3120w	3060w	3060m	ν(NH)
3000w	3015w	3000w	3025w	
2925w	2920w	2950w		ν(CH)
1515vs	1530vs	1530vs	1525vs	thioamide I
1300vs	1300s	1300vs	1300vs	thioamide II
1050vs	1040s	1040s	1020s	thioamide III
655vs	655s	655s	655s	thioamide IV
		560s		
	510vs	520s	520vs	ring
			510vs	skeletal
			490vs	ν(PC)
	460vs	460vs		
	420m		430m	

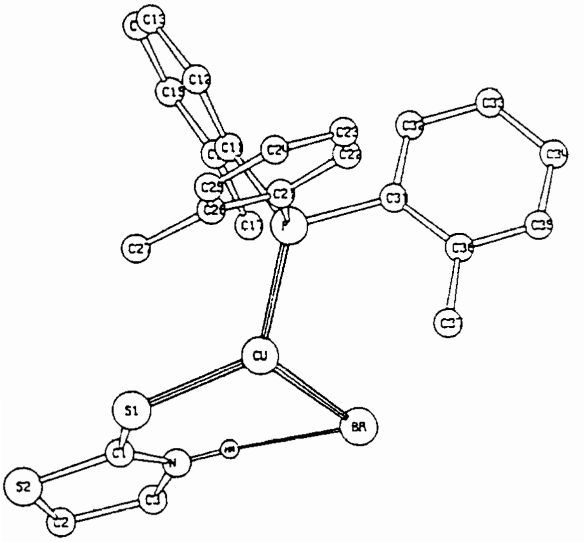

Fig. 1. A view of the complex. Thin lines denote N–H · · · Br hydrogen bonds.

mechanism of the complexes, on the grounds of the lability of the triphenylphosphine ligand in solution [2, 13–15]. Quantum yields have been determined at room temperature and they are reported in Table 3.

Description of the crystal structure

The structure of the [CuBr(totp)(tzdtH)] complex with the relevant atomic numbering is presented in Fig. 1.

The environment about the metal atom is three coordinate planar and involves a bromine atom, a sulfur atom from the tzdtH molecule and a phosphorus atom from totp.

Although the coordination number three is not the most favored configuration for Cu(I), it can be often realized, usually in conjunction with 'soft' ligands such as sulfur or phosphorus donors. The majority of known trigonal planar copper(I) complexes are cations of the type CuL_3^+, while the reported neutral complexes, usually of the formula CuL_2X, are still relatively rare. Most of these complexes are formed by bulky ligands, e.g. triphenylphosphine, phosphine sulfide, aromatic amines or thiones. This is not surprising since the steric hindrance plays a major role in stabilizing the coordination number three [16]. On the other hand, these typical π-acceptor ligands are capable of an appreciable multiple bonding to the d^{10} metal, thus electronic factors may be also of considerable significance.

For all that, during the course of our study on coordination of phosphines and heterocyclic thiones to Cu(I), we only have hitherto isolated several examples with tetrahedral coordination around copper. Therefore, the steric effect of the totp ligand must be the major controlling factor for the exception obtained in the present case, in particular the peculiar positioning of the three methyl groups surrounding copper.

Selected interatomic distances and bond angles are listed in Table 5. The Cu–S distance of 2.290(1) Å is significant longer than those found in other three coordinate copper(I) complexes [17, 18], but somewhat shorter than the similar interactions in the corresponding mixed ligand complexes [CuCl(tzdtH)(tptp)]$_2$ (2.386(1) Å) [4] and [CuCl(pymtH)(tptp)]$_2$ (2.356(1) Å) [2] with bridging Cu–S bonds. This shortening has been observed previously for the simple complexes of Cu(I) with heterocyclic thiones [17, 18] and can be attributed to the reduced steric repulsion around the trigonal copper atom, since the metal-to-ligand π-interaction according to such shortening must be of poor significance.

The Cu–P distance of 2.256(1) Å is comparable with the Cu–P distances in [Cu(PPh$_3$)$_2$Br] (av. 2.272(3) Å) [19], somewhat longer than that found in [CuCl(PPh$_3$)(pptu)] (2.206(4) Å [7] but within the range of those found in a number of four-coordinated copper(I) complexes [2–6, 20–22]. Consequently, a correlation between the Cu–P distance and the coordination number cannot exist, but steric repulsions appear to be of considerable importance in this case.

The Cu–Br bond length of 2.413(0) Å is within the range of values (2.32–2.52 Å) previously reported for Cu(I) complexes [16, 23] and seems to

TABLE 5. Interatomic distances (Å) and angles (°) for [Cu(totp)(tzdtH)Br][a]

Distances			
Cu–Br	2.413(0)	C15–C16	1.390(4)
Cu–P	2.256(1)	C16–C17	1.517(4)
Cu–S1	2.290(1)	C21–C22	1.405(4)
C1–S1	1.694(3)	C22–C23	1.378(4)
C1–S2	1.732(3)	C23–C24	1.376(5)
C1–N	1.304(4)	C24–C25	1.374(5)
C2–S2	1.807(4)	C25–C26	1.397(4)
C2–C3	1.514(5)	C26–C27	1.505(4)
C3–N	1.448(4)	C31–C32	1.394(4)
P–C11	1.844(3)	C31–C36	1.403(4)
P–C21	1.841(3)	C32–C33	1.380(4)
P–C31	1.835(3)	C33–C34	1.370(5)
C11–C12	1.391(4)	C34–C35	1.369(5)
C11–C16	1.404(4)	C35–C36	1.392(4)
C12–C13	1.382(4)	C36–C37	1.504(4)
C13–C14	1.372(5)		
C14–C15	1.363(5)		
Angles			
Br–Cu–P	116.9(0)	C11–C16–C15	118.2(3)
Br–Cu–S	113.4(0)	C11–C16–C17	122.4(3)
P–Cu–S1	125.8(0)	C15–C16–C17	119.4(3)
Cu–P–C11	113.7(1)	P–C21–C22	119.8(2)
Cu–P–C21	120.4(1)	P–C21–C26	121.1(2)
C11–P–C21	103.2(1)	C26–C21–C22	119.4(3)
Cu–P–C31	112.8(1)	C21–C22–C23	121.4(3)
C11–P–C31	102.7(1)	C22–C23–C24	119.2(3)
C21–P–C31	102.0(1)	C23–C24–C25	120.2(3)
Cu–S–C1	108.1(1)	C24–C25–C26	121.7(3)
S1–C1–S2	120.1(2)	C21–C26–C25	118.3(3)
S1–C1–N	127.9(2)	C21–C26–C27	122.2(3)
S2–C1–N	112.0(1)	C25–C26–C27	119.4(3)
C1–S2–C2	93.3(2)	P–C31–C32	121.1(2)
S2–C2–C3	107.3(2)	P–C31–C36	119.9(2)
C1–N–C3	119.1(3)	C32–C31–C36	119.0(2)
P–C11–C12	120.8(2)	C31–C32–C33	121.3(3)
P–C11–C16	120.6(2)	C32–C33–C34	119.7(3)
C12–C11–C16	118.7(2)	C33–C34–C35	119.7(3)
C11–C12–C13	121.5(3)	C34–C35–C36	122.3(3)
C12–C13–C14	119.5(3)	C31–C36–C35	117.9(3)
C13–C14–C15	119.7(3)	C31–C36–C37	123.0(3)
C14–C15–C16	122.4(3)	C35–C36–C37	119.0(3)

[a] e.s.d.s given in parentheses.

remain uninfluenced on changing the coordination number.

The contacts in the lattice Cu···S′ (3.199(1) Å) and Cu···Cu′ (4.229(6) Å), can hardly be considered as bonds [24].

The values of the angles are not significantly distorted from the idealized value of 120° in the nearly trigonal planar CuSPBr core.

As expected, the largest angle is P–Cu–S (125.8(0)°). This opening up may be greatly affected by the steric interactions between the two bulky ligands totp and tzdtH. The same effect was observed in the analogous complex {[1-phenyl-3-(2-pyridyl)-2-thiourea]copper(I)chloride} [7]. The small difference between the P–Cu–Br (116.9(0)° and Br–Cu–S (113.4(0)°) angles can be explained by an intramolecular Br···H–N hydrogen bond (Br···N = 3.286(4), N–H = 0.92(3), Br···H–N = 2.39(3) Å and N–H(N)···Br = 165(2)°).

The copper atom is displaced 0.263 Å from the plane of the bromine, sulfur and phosphorus atoms.

Supplementary material

Lists of observed and calculated structure factors, of positional and anisotropic thermal parameters of the H atoms and of the positional and equivalent thermal parameters of the phenyl-carbon atoms are available from the authors on request.

References

1 E. S. Raper, *Coord. Chem. Rev., 61* (1985) 115.

2 P. Karagiannidis, S. K. Hadjikakou, P. Aslanidis and A. Hountas, *Inorg. Chim. Acta, 178* (1990) 27.

3 P. Karagiannidis, P. Aslanidis, D. P. Kessisoglou, B. Krebs and M. Dartmann, *Inorg. Chim. Acta, 156* (1989) 47.

4 S. K. Hadjikakou, P. Aslanidis and P. Karagiannidis, A. Hountas and A. Terzis, *Polyhedron, 10* (1991) in press.

5 P. Karagiannidis, P. Aslanidis, S. Papastefanou, D. Mentzafos, A. Hountas and A. Terzis, *Inorg. Chim. Acta, 156* (1989) 277.

6 P. Karagiannidis, P. Aslanidis, S. Papastefanou, D. Mentzafos, A. Hountas, A. Terzis, *Polyhedron, 9* (1990) 71.

7 M. Belicchi Ferrari, G. Gasparri Fava, C. Pelizzi and P. Tarasconi, *Inorg. Chim. Acta, 97* (1985) 99.

8 *International Tables for X-ray Crystallography,* Vol. IV, Kynoch Press, Birmingham, U.K., 1974.

9 G. M. Sheldrick, *SHELX 76,* program for crystal structure determination, University of Cambridge, U.K., 1976.

10 N. Krishanaswami and D. Bhargava, *Indian J. Chem., 7* (1969) 710.

11 P. Klaboe, *Acta Chem. Scand., 22* (1968) 1532.

12 C. R. Saha and N. K. Roy, *J. Coord. Chem., 12* (1983) 165.

13 P. Aslanidis, P. Karagiannidis and S. Hadjikakou, *Book of Abstr., 1st Chemistry Conf. Cyprus–Greece, Sept. 23–27, 1988,* Nicosia, Cyprus, p. 90.

14 D. J. Fife, W. M. Moore and K. W. Morse, *Inorg. Chem., 23* (1984) 1545.

15 L. Pauling, in *The Nature of the Chemical Bond,* Cornel University Press, Ithaca, 3rd edn., 1960.

16 P. G. Eller, D. C. Bradley, M. B. Hursthouse and D. W. Meek, *Coord. Chem. Rev., 24* (1977) 1.

17 E. S. Raper, J. R. Creighton, W. Clegg and A. Milne, *Inorg. Chim. Acta, 149* (1988) 265.
18 S. C. Kokkou, S. Fortier, P. J. Rentzeperis and P. Karagiannidis, *Acta Crystallogr., Sect. C, 39* (1983) 178.
19 P. H. Davis, R. L. Belford and I. C. Paul, *Inorg. Chem., 12* (1973) 213.
20 P. Karagiannidis, P. Aslanidis, S. Papastefanou, D. Mentzafos, A. Hountas, A. Terzis, *Polyhedron, 9* (1990) 2833.
21 C. Lecomte, S. Skoulika, P. Aslanidis, P. Karagiannidis and S. Papastefanou, *Polyhedron, 8* (1989) 1103.
22 A. Aubry, S. Skoulika, P. Karagiannidis, P. Aslanidis and S. Papastefanou, *Inorg. Chim. Acta,* in press.
23 R. P. Shibaeva and V. F. Kaminkii, *Kristallografiya, 26* (1981) 332.
24 J. M. W. L. Birker, H. M. J. Hendricks and J. Reedijk, *Inorg. Chim. Acta, 55* (1982) L17.