Synthesis and Reactivity of the First Ag(I) Perthiocarboxylates. Crystal Structures of Tetra(*o*-tolylperthiocarboxylato)tetra-silver(I), $[AgS_3C\text{-}o\text{-tolyl}]_4$, and of its Cocrystallization Product with Copper(I), $[Ag_{1.76}Cu_{2.24}(S_3C\text{-}o\text{-tolyl})_4]$

NAZARIO MARSICH, GIORGIO PELLIZER, ANNAMARIA CAMUS*
Dipartimento di Scienze Chimiche, Università di Trieste, 34127 Trieste (Italy)
ANNA MARIA MANOTTI LANFREDI* and FRANCO UGOZZOLI
Istituti di Chimica Generale e Inorganica e di Strutturistica Chimica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze, 43100 Parma (Italy)

(Received August 22, 1989)

Abstract

Ag(I)-*o*-tolylperthiocarboxylate (I) and some Ag(I) arylperthiodithiocarboxylates were prepared by addition of $AgNO_3$ to the product isolated from reaction of aldehydes and ammonium polysulfide in basic medium. The X-ray diffraction analysis of I showed that its structure consists of tetranuclear $[Ag(S_3CC_7H_7)]_4$ complexes and is isomorphous with the corresponding Cu(I) derivative. Mixed crystals of the two pure molecular species, of microscopical structural uniformity, could be obtained. The X-ray diffraction analysis on a suitable crystal of these cocrystallized products yielded a formula $[Ag_{1.76}Cu_{2.24}(S_3CC_7H_7)_4]$ (II); the structure of II is isomorphous with the pure components. Crystals of I and II are both triclinic, space group $P\bar{1}$, with $a = 13.189(3)$, $b = 13.085(3)$, $c = 12.742(3)$ Å, $\alpha = 98.35(2)$, $\beta = 85.28(2)$, $\gamma = 75.71(2)°$ and $Z = 2$ for I; $a = 12.727(2)$, $b = 13.152(2)$, $c = 12.860(3)$ Å, $\alpha = 103.93(2)$, $\beta = 81.64(2)$, $\gamma = 84.72(2)°$ and $Z = 2$ for II. Final R and R_w were respectively 5.53 and 7.03 for I and 3.73 and 4.94 for II. The CS_3 group of the above compounds undergoes desulfuration by triphenylphosphine, giving, according to the stoichiometries of the reactions, the dithiocarboxylates or their complexes $AgS_2CAr(PPh_3)$ and $AgS_2CSAr(PPh_3)_2$. Some significant IR and NMR data for the above compounds are reported.

Introduction

Although several Cu(I) perthio [1–7] and dithio [5, 6, 8] carboxylates with interesting oligomeric structures have been studied in the last years, only a few silver(I) dithiocarboxylate compounds have been reported [9–11]. This paper deals with the preparation of the first Ag(I) perthiocarboxylate (I), of (Ag(I), Cu(I)) perthiocarboxylates and of Ag(I) perthiodithio complexes together with the crystal structure of I and of one of its cocrystallization products with copper(I), $[(Ag, Cu)S_3C\text{-}o\text{-}T]_4$ (*o*-T = *o*-tolyl) (II), where the Ag:Cu ratio is 0.44:0.56. Furthermore it reports a series of dithiocarboxylates, obtained by reacting the above compounds with triphenylphosphine.

Experimental

Materials

All chemicals and solvents were commercial products and were used as received, unless otherwise specified.

Preparation of the Complexes

Silver(I) perthiodithiocarboxylates *$[Ag_2(S_3CAr)(S_2CAr)]_n$ (Ar = Ph; p-T)*

A mixture of sulfur (2.0 g, 0.062 mol) and $(NH_4)_2S$ (9.5 ml of a C. Erba 20% solution, 0.028 mol) in 60 ml of THF was refluxed for 15 min and again for the same time after addition of 0.035 mol of ArCHO. The resulting red–brown solution was cooled at room temperature, diluted with 50 ml of water and extracted repeatedly with a total of 150 ml of Et_2O, to remove unreacted aldehyde and other organic by-products (disulfides). Solid sulfur, usually present, was filtered off from the aqueous solution and then $AgNO_3$ (2.5 g, 0.015 mol) in 30 ml of water was added slowly while stirring. After 3 h the dark red powder formed was filtered and thoroughly washed with water and a $MeOH\text{–}Et_2O$ 1:1 vol./vol. mixture. Yields of rough products: 3.5 g (77.5%) and 2.7 g (65%) respectively. The products were recrystallized from hot pyridine.

---

*Authors to whom correspondence should be addressed.

0020-1693/90/$3.50

Further addition of $AgNO_3$ to the mother liquors of the above preparations resulted in precipitation of $[AgS_2CAr]_n$ compounds.

A black solid, with approximate formula AgS, was obtained instead by adding the starting reagent mixture to an excess of $AgNO_3$.

Silver(I) dithiocarboxylates $[AgS_2CAr]_n$ *(Ar = Ph; p-T)*

A total of 0.090 g (0.34 mmol) of PPh_3 was added under stirring to a suspension of 0.34 mmol of the $[Ag_2(S_3CAr)(S_2CAr)]$ compound in 15 ml of pyridine. The colour of the suspension changed gradually from amaranth to deep brown. After 12 h the solid product was filtered, thoroughly washed with toluene and dried under vacuum. Recrystallization was from hot pyridine.

Silver(I) bis(triphenylphosphino)dithiocarboxylates $[AgS_2CAr(PPh_3)_2]$ *(Ar = Ph; p-T)*

An excess (0.950 g, 3.62 mmol) of PPh_3 was added to a suspension of 0.687 mmol of the perthiodithiocarboxylate in 30 ml of toluene. The red–violet solution, obtained at once, was filtered clear. From it crystals precipitated in practically quantitative yield upon dilution with petroleum ether (boiling point 30–50 °C). They were recrystallized from toluene–petroleum ether.

Silver(I) triphenylphosphino-p-tolyldithiocarboxylate

$[AgS_2C\text{-}p\text{-}T\cdot PPh_3]$ was obtained from the corresponding bis-triphenylphosphino complex by repeated crystallizations from carbon disulfide and petroleum ether.

The same product was obtained by stirring (24 h) a suspension of $[AgS_2C\text{-}p\text{-}T)_n$ in toluene with PPh_3 in Ag:P ratio = 1, at room temperature. The corresponding reaction with the phenyl derivative gave the bis(triphenylphosphino) complex and recovery of the Ag(I) phenyldithiocarboxylate in excess.

Silver(I)-o-tolylperthiocarboxylate $[AgS_3C\text{-}o\text{-}T]_n$

A mixture of $(NH_4)_2S$ (0.014 mol) and sulfur (1.5 g, 0.047 mol) in 60 ml of THF was refluxed for 15 min. After complete solubilization of sulfur, 0.017 mol of freshly distilled *o*-tolualdehyde was added and the solution refluxed again for 20 min. It was then diluted with 50 ml of water and extracted with 150 ml of Et_2O. The aqueous layer was filtered clear and treated drop by drop with an aqueous solution (20 ml) of 0.006 mol $AgNO_3$, under rapid stirring. The brown glue immediately formed was separated by decantation, washed repeatedly with water and dissolved in 50 ml of CH_2Cl_2. The red–brown solution, dried on Na_2SO_4, yielded after evaporation of the solvent, 1.2 g (66%) of a brown powder. Further purification (column chromatography on silica gel, eluent benzene–pyridine, 9:1 vol./vol. mixture) gave orange microneedles of pure product.

A brown–black band remained on the silica gel column. Elution with benzene–pyridine, 1:1 vol./vol. mixture, furnished a deep brown powder of scarcely reproducible composition. Its Ag:S ratio varied in different runs from 0.66 to 1, the IR spectra being always similar to that of the $[CuS_3C\text{-}p\text{-}T]_4$ compound, but for minor details and the broadening of some absorption bands.

(Silver(I),copper(I))-o-tolylperthiocarboxylates $[(Ag,Cu)S_3C\text{-}o\text{-}T]_n$

Two preparation methods were followed:

(i) CS_2 solutions of silver and copper perthiocarboxylates were mixed and the solvent evaporated slowly after some hours.

(ii) Pyridine solutions of copper *o*-tolylperthiocarboxylate and $AgNO_3$ were mixed, the black residue filtered off and the solvent evaporated.

Purification was by recrystallization from CS_2 and acetone or by chromatography on silica gel of a CS_2 solution (eluent CS_2–pyridine 9:1 vol./vol. mixture).

Products with an Ag:Cu ratio from 0.57:0.43 to 0.36:0.64 were isolated starting from equivalent amounts of the two metals, while a practically complete substitution of copper was obtained with large excess (3:1) of $AgNO_3$.

Silver(I)-o-tolyldithiocarboxylate $[AgS_2C\text{-}o\text{-}T]_n$

A solution of PPh_3 (0.385 g, 1.46 mmol) in 10 ml of toluene was added to a suspension of $AgS_3C\text{-}o\text{-}T$ (0.45 g, 1.46 meq Ag) in 20 ml of toluene. A gradual solubilization of the complex occurred, while a new dark orange crystalline product was formed. After 1 h of stirring the latter was filtered off, washed with toluene and dried under vacuum. A practically quantitative yield of a compound of correct elemental analysis was obtained. It could be recrystallized by slowly (days) evaporation from a pyridine–xylene mixture, giving well formed crystals of rough formula $AgS_2C\text{-}o\text{-}T\cdot py$, which correspond probably to the $[Ag_4(S_2C\text{-}o\text{-}T)_4py_4]$ complex [10, 11].

Silver(I) bis(triphenylphosphino)-o-tolyldithiocarboxylate·toluene solvate, $[AgS_2C\text{-}o\text{-}T(PPh_3)_2]\cdot C_7H_8$

A total of 0.300 g (1.14 mmol) of PPh_3 was added to a suspension of 0.100 g (0.325 mmol) of Ag(I)–*o*-tolylperthiocarboxylate in toluene (10 ml), under stirring. From the orange–red solution formed immediately, crystals of the new complex precipitated after few minutes. The solid was filtered off and washed with little toluene.

Silver(I) triphenylphosphino-o-tolyldithiocarboxylate [AgS_2C-o-T·PPh_3]

A total of 0.200 g (0.73 mmol) of PPh_3 was added to a suspension of 0.195 g of $[AgS_2C\text{-}o\text{-}T]_n$ (0.74 meq. Ag) in 25 ml of toluene. The solubility increased and the mother liquor assumed an orange–brown colour. After 12 h of stirring at room temperature, the solid was filtered out and washed with small amounts of toluene. More product was recovered from the mother liquor by addition of petroleum ether.

X-ray Data Collection and Refinement

An orange needle-shaped crystal of silver(I)-*o*-tolylperthiocarboxylate (**I**), of dimensions 0.20 × 0.28 × 0.34 mm, and a deep-red irregularly shaped crystal of (silver(I),copper(I))-*o*-tolylperthiocarboxylate (**II**), of dimensions 0.19 × 0.27 × 0.33 mm, were used for the X-ray analyses. Unit cell parameters were obtained by least-squares refinement of the θ values of 28 (**I**) and 30 (**II**) reflections, carefully measured on a Siemens AED (**I**) and on a Philips PW 1100 (**II**) single crystal diffractometer.

Complex **I**: $C_{32}H_{28}Ag_4S_{12}$, $M_r = 1228.77$, triclinic, $a = 13.189(3)$, $b = 13.085(3)$, $c = 12.742(3)$ Å, $\alpha = 98.35(2)$, $\beta = 85.28(2)$, $\gamma = 75.71(3)^\circ$, $V = 2092.3(9)$ Å^3, $Z = 2$, $D_c = 1.950$ g cm^{-3}, $F(000) = 1200$, Cu Kα radiation, $\bar{\lambda} = 1.54178$ Å, $\mu(\text{Cu K}\alpha) = 208.49$ cm^{-1}. Space group $P\bar{1}$ from structure determination.

Complex **II**: $C_{32}H_{28}Ag_{1.76}Cu_{2.24}S_{12}$, $M_r = 1129.48$, triclinic, $a = 12.727(2)$, $b = 13.152(2)$, $c = 12.860(3)$ Å, $\alpha = 103.93(2)$, $\beta = 81.64(2)$, $\gamma = 84.72(2)^\circ$, $V = 2048.9(7)$ Å^3, $Z = 2$, $D_c = 1.831$ g cm^{-3}, $F(000) = 1119$, Mo Kα radiation, $\bar{\lambda} = 0.71068$ Å, $\mu(\text{Mo K}\alpha) = 25.85$ cm^{-1}. Space group $P\bar{1}$ from structure determination.

Intensities were collected at room temperature using Ni-filtered Cu Kα radiation for **I** and graphite monochromatized Mo Kα radiation for **II** with θ–2θ scan technique. All the $\pm h \pm k\, l$ reflections in the range $3 \leqslant \theta \leqslant 55^\circ$ for **I** and $2.5 \leqslant \theta \leqslant 22^\circ$ for **II** were measured. Scan width from $[(\theta - 0.65)^\circ$ to $(\theta + 0.65 + \Delta\lambda/\lambda \text{ tg } \theta)^\circ]$ for both the data collections. Of 5542 (**I**) and 5428 (**II**) independent reflections, 2752 (**I**) and 2261 (**II**), having $I \geqslant 2\sigma(I)$, were considered observed and used in the analyses. Correction for absorption effects [12] were applied for both compounds using the program ABSORB [13] (max. and min. values for the absorption coefficients were 1.320 and 0.712 for **I** and 1.244 and 0.712 for **II**).

The structures were solved by direct and Fourier methods for both compounds and their refinements were carried out by blocked full-matrix least-squares using the SHELX system of computer programs [14]. First isotropic and then anisotropic thermal parameters were estimated for all the non-hydrogen atoms of both compounds. For **II** metal atom occupancies were included as variables and gave values consistent with 46%, 26%, 64%, 40% for silver and 54%, 74%, 36%, 60% for copper at M(1), M(2), M(3), M(4) metal atom positions respectively. The hydrogen atoms of both compounds were placed at their geometrically calculated positions and introduced in the final structure-factor calculations.

The weighting scheme used in the last cycles of refinements was $w = K[\sigma^2(F_o) + gF_o]$ with $K = 0.3399$ and $g = 0.0076$ for **I** and $K = 0.1589$ and $g = 0.0083$ for **II**. Final R and R_w were respectively 5.53 and 7.03 for **I** and 3.73 and 4.94 for **II**. Atomic scattering factors, corrected for the anomalous dispersion of Ag, Cu and S, were taken from ref. 15. Final atomic coordinates for the non-hydrogen atoms are given in Tables 1 and 2 for **I** and **II** respectively.

All the calculations were performed on a GOULD POWERNODE of the Centro di Strutturistica Diffrattometrica del C.N.R. Parma.

Results

To prepare copper(I) perthiocarboxylates we had found the reaction between ammonium perthiocarboxylate and a water soluble copper(II) salt useful [4, 5]. The only Ag(I) perthiocarboxylate isolated in the corresponding reaction with $AgNO_3$, was the *o*-tolyl compound. The phenyl and *p*-tolyl derivatives gave perthiodithio complexes, as already found with Ni(II), Pd(II) and Pt(II) by the same method [16]. The first reagent hence seems to be a mixture of perthio and dithio salts and the isolation of pure Ag(I) perthio-*o*-tolylcarboxylate succeeded because, like in the corresponding copper(I) derivative [4], the perthiodithio-*o*-tolyl compound does not form.

As reported in the experimental part, $[AgS_2CAr]_n$ were by-products of the above reactions, but they could be prepared more conveniently by reacting the perthio or perthiodithio compounds with one triphenylphosphine molecule for each CS_3 group. The triphenylphosphine extracts a sulfur atom from the latter group, giving PPh_3S. With more triphenylphosphine the formed Ag(I) dithiocarboxylates reacted in turn, giving two series of complexes: $[(AgS_2CAr)PPh_3]_n$ and $[AgS_2CAr(PPh_3)_2]$. The latter are stable in solution in excess triphenylphosphine, but dissociate in pure solvents. A CS_2 solution of the *p*-tolyl derivative, for example, separated in a short time the less soluble monophosphine complex, while in hot toluene both the PPh_3 molecules were removed from the same compound, with precipitation of the parent dithiocarboxylate.

Complexes corresponding to the tetranuclear and easily isolated $[(CuS_2CAr)_4(PPh_3)_2]$ compounds [8], could not be obtained with silver. Attempts to get these complexes for phenyl- and *p*-tolyldithiocarboxylates by metathesis between the corresponding copper(I) derivatives and $AgNO_3$, gave the silver dithiocarboxylates and $AgS_2CAr(PPh_3)_2$ complexes.

TABLE 1. Fractional atomic coordinates (×10^4) for the non-hydrogen atoms with e.s.d.s in parentheses for **I**

Atom	x/a	y/b	z/c
Ag(1)	4627(1)	528(1)	3724(1)
Ag(2)	2137(1)	1499(1)	4058(1)
Ag(3)	3507(1)	752(1)	1681(1)
Ag(4)	3395(1)	2896(1)	3172(1)
S(1)	3365(4)	531(4)	5245(4)
S(2)	3245(4)	−997(4)	4842(4)
S(3)	1724(4)	−165(4)	3326(4)
S(4)	1564(4)	3436(4)	4247(4)
S(5)	1898(5)	3966(4)	5727(4)
S(6)	4176(5)	3501(5)	4766(5)
S(7)	4852(4)	−815(3)	1954(4)
S(8)	6119(4)	−520(3)	1136(4)
S(9)	5819(4)	1429(3)	2855(4)
S(10)	3965(4)	2491(3)	1247(4)
S(11)	2681(4)	3175(4)	598(4)
S(12)	1720(4)	1460(4)	1272(5)
C(1)	2433(14)	−1090(14)	3899(13)
C(2)	2364(16)	−2241(13)	3650(14)
C(3)	3267(17)	−2950(14)	3058(16)
C(4)	3274(21)	−4049(17)	2775(21)
C(5)	2431(27)	−4349(16)	3109(21)
C(6)	1527(23)	−3637(18)	3681(20)
C(7)	1497(16)	−2548(14)	3977(17)
C(8)	548(20)	−1805(19)	4642(27)
C(9)	3158(16)	3975(14)	5749(14)
C(10)	3397(15)	4416(16)	6822(17)
C(11)	3759(19)	3756(18)	7518(20)
C(12)	4015(21)	4114(25)	8519(23)
C(13)	3920(19)	5198(26)	8779(22)
C(14)	3569(18)	5892(17)	8063(20)
C(15)	3281(17)	5520(17)	7067(18)
C(16)	2893(22)	6257(18)	6316(21)
C(17)	6379(14)	619(11)	1708(13)
C(18)	7234(15)	896(15)	1067(17)
C(19)	6944(17)	1344(15)	154(17)
C(20)	7673(25)	1633(19)	−463(25)
C(21)	8672(30)	1519(21)	−257(26)
C(22)	8986(19)	1072(22)	635(26)
C(23)	8208(21)	754(20)	1355(21)
C(24)	8577(16)	213(22)	2304(23)
C(25)	1746(14)	2527(13)	702(15)
C(26)	817(15)	3032(14)	172(19)
C(27)	954(21)	2867(19)	−924(20)
C(28)	154(23)	3311(23)	−1484(27)
C(29)	−782(29)	3942(24)	−919(27)
C(30)	−946(21)	4126(18)	160(28)
C(31)	−138(19)	3645(16)	743(20)
C(32)	−237(22)	3837(22)	1967(22)

TABLE 2. Fractional atomic coordinates (×10^4) for the non-hydrogen atoms with e.s.d.s in parentheses for **II**[a]

Atom	x/a	y/b	z/c
M(1)	1371(1)	420(1)	546(1)
M(2)	948(1)	2752(1)	1414(1)
M(3)	3251(1)	1540(1)	805(1)
M(4)	1795(1)	1624(1)	2865(1)
S(1)	−93(3)	1551(4)	566(3)
S(2)	220(3)	1678(3)	−1000(3)
S(3)	1636(3)	3259(3)	−87(3)
S(4)	844(3)	3333(3)	3207(3)
S(5)	−658(3)	3090(3)	3830(3)
S(6)	368(3)	866(3)	3524(3)
S(7)	3016(3)	255(3)	−743(3)
S(8)	3892(3)	−1019(3)	−494(3)
S(9)	2088(2)	−831(3)	1353(3)
S(10)	3596(3)	1061(3)	2510(3)
S(11)	4281(3)	2311(3)	3228(3)
S(12)	3774(3)	3235(3)	1394(3)
C(1)	1084(9)	2577(10)	−1072(9)
C(2)	1353(8)	2644(10)	−2226(8)
C(3)	1956(9)	1752(10)	−3009(10)
C(4)	2185(11)	1814(12)	−4074(11)
C(5)	1841(11)	2719(13)	−4352(10)
C(6)	1259(10)	3594(12)	−3621(11)
C(7)	1001(9)	3563(10)	−2512(10)
C(8)	338(14)	4483(11)	−1709(12)
C(9)	−633(10)	1815(10)	3897(10)
C(10)	−1743(11)	1603(10)	4392(13)
C(11)	−2424(13)	1280(12)	3658(15)
C(12)	−3436(14)	1033(12)	4069(17)
C(13)	−3680(13)	1145(13)	5211(19)
C(14)	−2972(15)	1491(12)	5908(13)
C(15)	−1976(12)	1730(11)	5522(12)
C(16)	−1232(15)	2090(19)	6266(14)
C(17)	3262(8)	−1369(8)	617(9)
C(18)	3900(10)	−2202(9)	893(10)
C(19)	4814(11)	−1976(11)	1313(10)
C(20)	5433(12)	−2733(17)	1633(12)
C(21)	5130(18)	−3764(15)	1461(15)
C(22)	4240(16)	−3984(15)	1018(15)
C(23)	3623(12)	−3226(12)	724(10)
C(24)	2688(15)	−3540(15)	210(18)
C(25)	4238(9)	3240(9)	2518(9)
C(26)	4805(12)	4138(10)	3025(10)
C(27)	5915(13)	4004(14)	2914(11)
C(28)	6467(13)	4818(16)	3356(15)
C(29)	5884(18)	5730(15)	3963(13)
C(30)	4817(16)	5864(13)	4093(12)
C(31)	4245(12)	5091(11)	3631(10)
C(32)	3059(13)	5274(12)	3800(14)

[a] In II metal site M(1) was 46% Ag and 54% Cu, M(2) was 26% Ag and 74% Cu, M(3) was 64% Ag and 36% Cu and M(4) was 40% Ag and 60% Cu.

Like its Cu(I) analogue, $[AgS_2C\text{-}o\text{-}T]_n$, refluxed in toluene with sulfur, gave the perthiocarboxylate. Under these conditions the phenyl and *p*-tolyl derivatives formed the above perthiodithio compounds and the same products were obtained also by reacting in pyridine phenyl- and *p*-tolylperthio copper(I) with $AgNO_3$. $CuS_3C\text{-}o\text{-}T$ with $AgNO_3$ gave a series of (Ag(I),Cu(I))-*o*-tolylperthiocarboxylates, in which both metals are present in unique crystalline phases, whose solubilities and IR spectra were different from those of solid mixtures of the two parent compounds.

TABLE 3. Analytical data of the compounds

Compound[a] (colour)	Decomposition point	Analyses (%)[b]			
		C	H	Ag	S
$[Ag_2(S_3CPh)(S_2CPh)]$ amaranth	216–220	29.6 (30.34)	1.9 (1.82)	38.0 (38.92)	29.0 (28.92)
$[AgS_2CPh]$ deep brown	216–218	31.8 (32.20)	2.3 (1.93)	41.6 (41.31)	24.5 (24.56)
$[AgS_2CPh(PPh_3)_2]$ violet	178–180	65.4 (65.73)	4.35 (4.49)	13.5 (13.73)	8.2 (8.16)
$[AgS_3C\text{-}o\text{-}T]_4$ orange	167–169	31.5 (31.28)	2.45 (2.30)	34.9 (35.11)	31.0 (31.3)
$[AgS_2C\text{-}o\text{-}T]$ orange–red	204–206[c]	35.0 (34.92)	2.5 (2.57)	38.9 (39.21)	23.4 (23.31)
$[AgS_2C\text{-}o\text{-}T(PPh_3)_2]\cdot$Tol. red–violet[d]	181–183	68.1 (68.68)	4.9 (5.09)	12.0 (12.10)	7.3 (7.19)
$[AgS_2C\text{-}o\text{-}T\cdot PPh_3]$ orange	194–196	(58.10)	(4.13)	19.9 (20.07)	(11.93)
$[Ag_2(S_3C\text{-}p\text{-}T)(S_2C\text{-}p\text{-}T)]$ amaranth	218–219	32.8 (33.00)	2.5 (2.42)	37.1 (37.05)	27.5 (27.53)
$[AgS_2C\text{-}p\text{-}T]$ brown–violet	213–214	35.3 (34.92)	2.7 (2.57)	39.5 (39.21)	22.9 (23.31)
$[AgS_2C\text{-}p\text{-}T(PPh_3)_2]$ violet	165–166	66.3 (66.08)	4.8 (4.66)	13.4 (13.49)	7.9 (8.02)
$[AgS_2C\text{-}p\text{-}T\cdot PPh_3]$ green–brown	201–202	58.9 (58.10)	4.0 (4.13)	20.1 (20.07)	11.9 (11.93)

[a] Minimal formulae are given for compounds, whose structures were not confirmed by X-ray diffraction methods. [b] Calculated values in parentheses. [c] Decomposition point notably different from the melting point of a compound of the same composition previously reported [11], which could have a different nuclearity. [d] Became gradually orange by heating. Crystallization from CS_2 and petroleum ether gave a non-solvated orange complex, which did not show significant variations in the IR spectrum.

The products isolated and some of their characteristics are shown in Table 3. All the compounds are intensely coloured and, except for the phosphino complexes and the *o*-tolylperthiocarboxylate, practically insoluble in all common solvents but pyridine.

The solubility of the *o*-tolylperthiocarboxylate depends on the history of the sample and decreases on crystallization, while the colour changes from ochre to orange to red. The minor variations of the percentage composition and of the IR spectra, suggest the possibility of different degrees of polymerization for this compound. The only crystals suitable for X-ray analysis corresponded, for both Ag(I) pure and Ag(I),Cu(I) mixed complexes, to a tetranuclear form like in the copper(I) compound [4]. The original solubility of the Ag(I)-*o*-tolylperthiocarboxylate can be restored by recrystallization from pyridine. Molecular weight measurements showed that in this solvent the compound is monomeric at infinite dilution, the molecular weight increasing in the range of tested concentrations (0.3–2.0% wt./wt.) towards the formation of the dimer. The *o*-tolyldithiocarboxylate showed also an increase of molecular weight with increasing concentration, the values obtained suggesting also in this case the presence of monomeric species in diluted and of dimeric species in nearly saturated solutions (about 1.4% wt./wt.)*.

The very low solubilities of the perthiodithio compounds allowed measurements only in extremely dilute solutions, where they seem to dissociate giving mononuclear forms. In the solid state the silver atom of these compounds should instead be coordinated to four sulphur atoms, a full coordination state being suggested for these complexes by the absence of pyridine of crystallization, as Ag atoms bonded by only three sulfur atoms usually coordinate further with this solvent [10].

The complexes with triphenylphosphine showed in toluene (37 °C) molecular weights lower than the theoretical for mononuclear forms, confirming that dissociation of triphenylphosphine occurs easily, in particular for *p*-tolyl derivatives. The complexes were more stable in dichloroethane, notwithstanding a higher experimental temperature (45 °C).

---

*In the solid state Ag(I)-*o*-tolyldithiocarboxylate gives a tetrameric pyridine solvate $[(AgS_2C\text{-}o\text{-}T)_4py_4]$ [10, 11].

Crystal Structures of I and II

The molecular structures of **I** and **II** consist of discrete tetramers, [AgS$_3$C-*o*-T]$_4$ and [(Ag,Cu)S$_3$C-*o*-T]$_4$ respectively, represented in Figs. 1 and 2, with the relative atomic numbering scheme. Selected bond distances and angles are given in Table 4 for both **I** and **II**. The metal arrangement is very similar in the two compounds and consists of a tetrahedron, of silver atoms in **I** and of silver/copper cocrystallized atoms in **II**, with the four edges bridged by the terminal perthio atom from four *o*-tolylperthiocarboxylate ligands, shorter [3.026(2)–3.183(2) Å in **I** and 2.910(2)–2.976(2) Å in **II**] than the other M–M distances [3.281(2)–3.327(2) Å in **I** and 3.101(2)–3.169(2) Å in **II**]. MSSCS pentaatomic chelate rings (M = Ag in **I** and M = Ag, Cu in **II**) are formed as a consequence of the coordination of the other terminal sulfur atom of each ligand to only one metal atom. As already pointed out in similar cases [5, 8, 11] the shorter metal–metal distances, imposed by the stereochemical demand of the bridging ligands, are indicative of only soft metal attractive interaction so that each metal atom displays, in both compounds, a distorted trigonal geometry, with the three sulfur atoms roughly coplanar with the metal (the displacements of the metal atoms from the plane passing through the sulfur atoms being 0.105(2), −0.0172(2), −0.0157(2) and 0.215(2) Å for Ag(1), Ag(2), Ag(3) and Ag(4) in **I** and 0.005(2), −0.151(2), −0.210(2) and 0.200(2) Å for M(1), M(2), M(3) and M(4) in **II**).

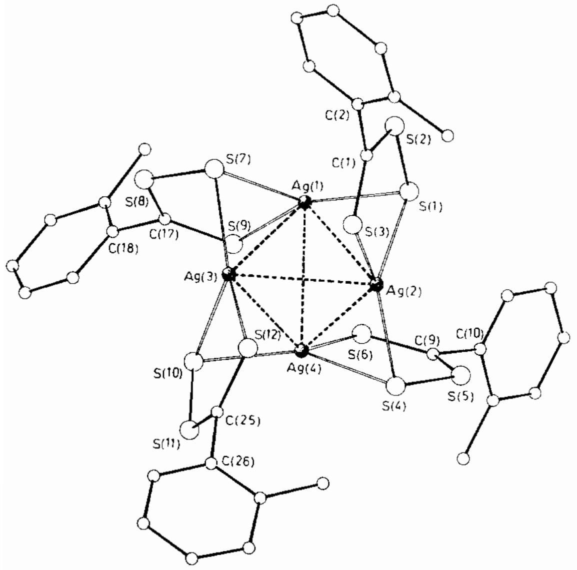


Fig. 1. Perspective view of the tetranuclear [AgS$_3$C-*o*-tolyl]$_4$ complex (I) with the labelling scheme.

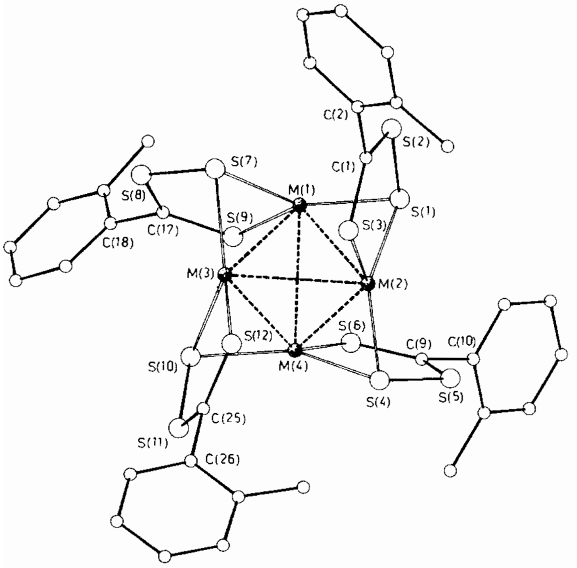


Fig. 2. Perspective view of the tetranuclear [MS$_3$C-*o*-tolyl]$_4$ (M = Ag, Cu) complex (II), showing labelling scheme. Metal site M(1) was 46% Ag and 54% Cu, M(2) was 26% Ag and 74% Cu, M(3) was 64% Ag and 36% Cu and M(4) was 40% Ag and 60% Cu.

The structures of **I** and **II** are very similar to that of the analogous copper(I) complex, [CuS$_3$C-*o*-T]$_4$ (**III**) [4], so **I**, **II** and **III**, which all crystallize in the space group $P\bar{1}$, form an isomorphous series of crystals.

Table 5 compares the weighted mean values of selected bond distances and angles in the three isomorphous compounds. All the bond distances and angles involving the metal atom in the Ag/Cu mixed complex are significantly different from the corresponding ones in both pure complexes, with values intermediate between those found for these latter compounds, although the variation is not linear. Only the S–M–S angles involving perthio atoms from adjacent ligands seem to be unaffected by the different metal sizes.

The MSSCS (M = Ag in **I**, M = Ag, Cu in **II**) chelate rings, which are roughly planar in both **I** and **II** complexes, are tilted to each other consecutively by angles ranging from 78.4(1) to 86.3(1)° in **I** and from 82.4(1) to 89.4(1)° in **II**. The corresponding angles in the Cu compound [4] range from 84.0(1) to 88.8(2)°. The dihedral angles the *o*-tolyl moieties form with the five-membered chelate rings, individuated by the progressively numbered metal atoms, are 71.0(6), 71.8(5), 77.0(7) and 85.7(6)° in **I** and 68.4(3), 68.5(3), 77.9(4) and 89.5(4)° in **II**. The corresponding dihedral angles are 65.3(2), 68.2(2), 80.2(2) and 89.3(3)° in **III**, the largest angles being associated, for all three isomorphous compounds, with the *o*-tolyl moieties with facing methyl groups on the C(16) and C(32) atoms.

By structural features of **I**, **II** and **III**, a degree of steric control of aggregation seems to be introduced in this series of compounds by the *o*-tolylperthiocarboxylate ligand. Already it has been pointed out

TABLE 4. Relevant bond distances (A) and angles (°) in I and II

	Compound			Compound	
	I (M = Ag)	II^a (M = Ag, Cu)		I (M = Ag)	II^a (M = Ag, Cu)
M(1)–M(2)	3.183(2)	2.969(2)	M(2)–S(1)	2.542(5)	2.327(5)
M(1)–M(3)	3.112(2)	2.941(2)	M(2)–S(3)	2.447(6)	2.274(4)
M(1)–M(4)	3.327(2)	3.169(2)	M(2)–S(4)	2.429(5)	2.228(4)
M(2)–M(3)	3.281(2)	3.101(2)	M(3)–S(7)	2.447(5)	2.357(5)
M(2)–M(4)	3.026(2)	2.910(2)	M(3)–S(10)	2.615(5)	2.508(5)
M(3)–M(4)	3.115(2)	2.976(2)	M(3)–S(12)	2.439(6)	2.365(4)
M(1)–S(1)	2.448(5)	2.268(5)	M(4)–S(4)	2.557(5)	2.362(4)
M(1)–S(7)	2.597(5)	2.432(4)	M(4)–S(6)	2.468(7)	2.303(4)
M(1)–S(9)	2.469(6)	2.332(4)	M(4)–S(10)	2.446(5)	2.287(4)
S(1)–S(2)	2.039(8)	2.045(6)	S(7)–S(8)	2.044(8)	2.042(6)
S(2)–C(1)	1.685(19)	1.697(14)	S(8)–C(17)	1.688(17)	1.717(12)
S(3)–C(1)	1.638(18)	1.652(12)	S(9)–C(17)	1.671(15)	1.643(10)
S(4)–S(5)	2.034(8)	2.047(5)	S(10)–C(11)	2.012(7)	2.021(6)
S(5)–C(9)	1.667(22)	1.697(14)	S(11)–C(25)	1.667(21)	1.694(14)
S(6)–C(9)	1.686(19)	1.629(12)	S(12)–C(25)	1.671(19)	1.638(13)
M(3)–M(1)–M(4)	57.7(1)	58.2(1)	M(2)–S(1)–S(2)	101.2(3)	101.3(2)
M(2)–M(1)–M(4)	55.3(1)	56.5(1)	S(1)–S(2)–C(1)	111.6(7)	109.0(5)
M(2)–M(1)–M(3)	62.8(1)	63.3(1)	M(2)–S(3)–C(1)	105.5(7)	104.5(5)
M(1)–M(2)–M(4)	64.8(1)	65.2(1)	S(2)–C(1)–S(3)	130.6(11)	128.3(8)
M(1)–M(2)–M(3)	57.5(1)	57.9(1)	S(3)–C(1)–C(2)	120.4(13)	122.2(9)
M(3)–M(2)–M(4)	59.0(1)	59.3(1)	S(2)–C(1)–C(2)	108.9(12)	109.4(8)
M(1)–M(3)–M(2)	59.7(1)	58.8(1)	M(2)–S(4)–S(5)	104.0(3)	104.0(2)
M(2)–M(3)–M(4)	56.4(1)	57.2(1)	S(4)–S(5)–C(9)	113.1(7)	109.3(5)
M(1)–M(3)–M(4)	64.6(1)	64.8(1)	M(4)–S(6)–C(9)	105.4(8)	104.9(5)
M(2)–M(4)–M(3)	64.6(1)	63.6(1)	S(5)–C(9)–S(6)	129.1(12)	129.0(9)
M(1)–M(4)–M(3)	57.7(1)	57.1(1)	S(6)–C(9)–C(10)	117.4(15)	119.9(10)
M(1)–M(4)–M(2)	59.9(1)	58.3(1)	S(5)–C(9)–C(10)	113.4(15)	111.1(10)
S(7)–M(1)–S(9)	89.3(2)	93.0(1)	M(1)–S(7)–S(8)	100.8(2)	101.6(2)
S(1)–M(1)–S(9)	148.8(2)	145.4(2)	S(7)–S(8)–C(17)	112.0(6)	110.3(4)
S(1)–M(1)–S(7)	121.3(2)	121.6(2)	M(1)–S(9)–C(17)	106.3(6)	107.6(4)
S(3)–M(2)–S(4)	143.9(2)	136.7(2)	S(8)–C(17)–S(9)	129.1(11)	126.5(7)
S(1)–M(2)–S(4)	123.4(2)	124.9(2)	S(9)–C(17)–C(18)	118.4(12)	121.0(9)
S(1)–M(2)–S(3)	91.1(2)	97.0(2)	S(8)–C(17)–C(18)	112.5(12)	112.5(8)
S(10)–M(3)–S(12)	89.0(2)	91.9(1)	M(3)–S(10)–S(11)	101.3(3)	101.3(2)
S(7)–M(3)–S(12)	147.1(2)	143.6(2)	S(10)–S(11)–C(25)	111.8(7)	110.1(5)
S(7)–M(3)–S(10)	122.5(2)	121.8(2)	M(3)–S(12)–C(25)	106.1(7)	105.8(5)
S(6)–M(4)–S(10)	134.9(2)	131.0(2)	S(11)–C(25)–S(12)	130.2(12)	130.2(8)
S(4)–M(4)–S(10)	131.9(2)	130.8(2)	S(12)–C(25)–C(26)	119.4(14)	120.1(9)
S(4)–M(4)–S(6)	90.8(2)	95.8(2)	S(11)–C(25)–C(26)	110.5(13)	109.5(9)

[a] For II metal site M(1) was 46% Ag and 54% Cu, M(2) was 26% Ag and 74% Cu, M(3) was 64% Ag and 36% Cu and M(4) was 40% Ag and 60% Cu.

the significant stereochemical influence of thiolate derivatives in determining structure and degree of aggregation in neutral silver(I) compounds [17].

The anisotropic thermal parameters of all the metal-bonded sulfur atoms are significant different in the pure complexes with respect to that in the mixed compound (B_{eq} ranging from 3.7(2) to 4.9(2) Å^2 in I and from 4.6(1) to 7.4(2) Å^2 in II). The increase of the atomic displacements of the metal-bonded S atoms in II could suggest a certain degree of disorder of the latter. But the analysis of the electron density difference map has not evidenced the presence of other peaks close to the sulfur atom sites. So we can hypothesize that the metal-bonded sulfur atom sites are uniformly singly occupied and not occupied by a weighted combination of sulfur atoms, one bonded to Cu and the other one bonded to Ag. Therefore, the lattice in II is not formed by a mixture of microscopically different structures but possesses microscopic uniformity. Concluding, the X-ray diffraction analysis confirms, as suggested by the IR spectra, the existence of the mixed Ag/Cu compounds, one of the rare cases in which the crystals have structural uniformity [18].

TABLE 5. Mean values of the relevant bond distances (Å) and angles (°), with their e.s.d.s in parentheses, of the isomorphous MS_3C-*o*-tolyl$_4$ compounds **I** (M = Ag), **II** (M = Ag, Cu) and **III** (M = Cu) [4]

	I	II	III
M–S[a]	2.578(3)	2.405(2)	2.275(1)
M–S[b]	2.443(3)	2.287(2)	2.236(1)
M–S	2.457(3)	2.319(2)	2.233(2)
S–S	2.031(4)	2.040(3)	2.050(1)
C–S[a]	1.680(10)	1.703(5)	1.710(4)
C–S	1.669(8)	1.649(4)	1.640(5)
S–M–S[c]	90.1(1)	93.2(1)	99.0(1)
S–M–S[d]	124.8(1)	124.8(1)	125.5(1)
S–M–S	143.7(1)	139.2(1)	133.3(1)
S–C–S	129.8(1)	128.3(4)	127.4(3)
C–C–S[e]	119.0(1)	119.9(1)	121.5(3)
C–C–S	111.1(1)	111.1(1)	111.1(1)

[a] Bond distance to the perthio sulfur atom in the MSSCS chelate ring. [b] Bond distance to the perthio sulfur atom of the adjacent MSSCS chelate ring. [c] Bite angle in the MSSCS chelate ring. [d] Bond angle involving perthio sulfur atoms from two adjacent MSSCS chelate rings. [e] Bond angle involving perthio surfur atom.

Cocrystallization, as solid solution, most commonly occurs in ionic systems where similar cations or anions may substitute one another in the lattice of a host complex. Examples of crystallographic studies showing that two 'pure' molecular species of intrinsically different steric demands are isomorphous and so are their molecular solutions, continue to be extremely rare. In particular 'cluster' compounds containing two different coniage metals are rather rare [19]; a single similar example of partial replacement of silver by copper atoms was recently reported for a thiolate anionic cluster [20].

As far as we know, the only structural study showing the microscopic structural uniformity of the mixed crystals with respect to the 'pure' molecular species, is represented by the above mentioned work on Cr/Zn saccharinates compounds [18]. While in these latter complexes the isostructural uniformity seems to be due to the energetic requirements of an extensive network of hydrogen bonds linking the molecules, our results could be attributable to the steric hindrance control of the ligands.

IR Spectra

Information about the mode of binding of the CS_3 and CS_2 groups can be obtained by comparison between IR spectra of silver(I) and copper(I) derivatives of known structure. Silver and copper *o*-tolylperthiocarboxylates, e.g., with corresponding tetranuclear crystal structures, show spectra with the same pattern, in which the characterizing absorption bands are also in extremely good agreement (Ag, $\nu(CS_2)$ 1023 and 886; $\nu(SS)$ 494; Cu, $\nu(CS_2)$ 1020 and 896; $\nu(SS)$ 486 cm^{-1}). The similarity of the IR spectra reflects, probably, more the mode of binding than the nuclearity of the compounds, because only minor spectral variations were observed for samples of Ag(I)-*o*-tolylperthiocarboxylate of markedly different physical properties and supposed of different degree of polymerization. The mixed silver–copper perthiocarboxylates show spectra very similar to the above ones, little but significant differences in the pattern being however present, suggesting that the products are not mixtures of the two.

The *o*-tolyldithiocarboxylates of silver and copper showed spectra of rather good correspondence, but for a shift to higher frequencies of the first absorption peak of CS_2 (Ag, 1021; Cu, 1003 cm^{-1}) and a reduction in the relative intensity of the $\nu(CS_2)$sym to about 900 cm^{-1}, in the silver compound.

In the spectra of the $[Ag_2(S_3CAr)(S_2CAr)]$ compounds (Ar = Ph, *p*-T) the main absorption peaks of the CS_3 and CS_2 groups are shifted by about 20 and 10 cm^{-1} respectively towards higher frequencies and the whole spectra show significant differences from those of the corresponding Cu(I) derivatives.

In the phenyl- and *p*-tolyl-Ag(I) dithiocarboxylates the main frequencies of $\nu(CS_2)$ (Ph, 1001s,br; *p*-T, 1016s cm^{-1}) are almost unaltered in comparison with those of the Cu(I) compounds, but the general patterns, dramatically different for the Ag(I) and Cu(I) derivatives, are consistent with their different basic structure: an infinite linear chain for the silver [10] and a discrete tetranuclear cluster for the copper compounds [5], with different coordination numbers of the metal atoms and a different binding mode of the CS_2 group (Scheme 1).

The spectra of the bis(triphenylphosphine) complexes, *o*-tolyl included, show again a perfect correspondence between silver and copper compounds*; those of the monotriphenylphosphine derivatives are characterized by a triplet of absorptions in the 500 cm^{-1} region.

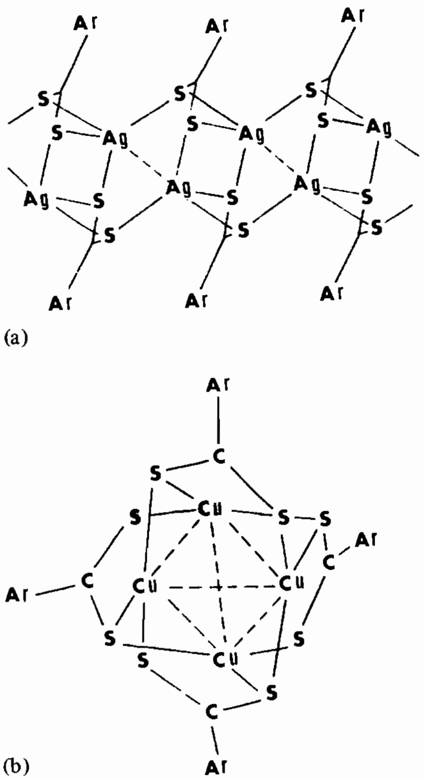
NMR Spectra

Due to the poor solubility of the above compounds, NMR spectra could be run in solvents different from d_5-pyridine only for the *o*-tolylperthiocarboxylate and the complexes with phosphine.

^1H and ^{13}C spectra of these compounds compare well with the ones previously obtained from the corresponding Cu(I) derivatives [21, 22]. Noticeably in the ^{13}C spectra for $[AgS_3C$-*o*-$T]_4$ in $CDCl_3$ the CS_3

---

*As suggested by this similarity mixed $(Ag,Cu)S_2CAr(PPh_3)_2$ (Ar = Ph, *o*-T) were obtained by reaction of mixtures of CuS_2CAr and AgS_2CAr with triphenylphosphine. Metathesis of $CuS_2CAr(PPh_3)_2$ complexes with $AgNO_3$ is not a good preparation method, because the main product of the reaction is the $[Cu(PPh_3)_2]NO_3$ complex.



Scheme 1.

resonance appeared at $\approx$230 ppm (231.1 for [CuS_3C-o-T]$_4$ in d_6-acetone-CS_2) and for $AgS_2CPh(PPh_3)_2$ and AgS_2C-p-$T(PPh_3)_2$ the CS_2 resonance appeared at 251.1 and 250.5 ppm respectively (248.5 and 248.0 for the corresponding copper complexes), hence confirming that chelating CS_2 is significantly deshielded [22].

Room temperature ^{31}P spectra of $AgS_2CAr(PPh_3)$ and $AgS_2CAr(PPh_3)_2$ complexes in $CDCl_3$ consist of one broadened resonance even in the presence of excess phosphine. Under corresponding conditions ^{31}P is less shielded in Ag than in Cu derivatives. The deshielding is even more marked in corresponding Au(I) compounds [21]. A preliminary study of the dependence of the shift on excess PPh_3 shows that in these solutions, at room temperature, free triphenylphosphine is in equilibrium with more than one complex species.

Acknowledgements

We are grateful to the Italian MPI for support of this work. We thank Dr E. Cebulec for C, H and S analyses and Mr P. de Baseggio for recording the IR spectra.

References

1 Tang Kaluo, Gan Hong, Xu Xiaojie, Zhou Gongdu and Tang Youqi, *Sci. Sin., Ser. B (Engl. Ed.)*, *27* (1984) 456.

2 Jin Xianglin, Jin Yi-Yan, Tang Kaluo and Tang Youqi, *Ziran Zazhi, 8* (1985) 919; *Sci. Sin., Ser. B, 3* (1987) 225.

3 Jin Xianglin, Jin Yi-Yan and Tang Youqi, *Acta Chim. Sin., 44* (1986) 580.

4 A. M. Manotti Lanfredi, A. Tiripicchio, N. Marsich and A. Camus, *Inorg. Chim. Acta, 142* (1988) 269.

5 A. Camus, N. Marsich, A. M. Manotti Lanfredi and F. Ugozzoli, *Inorg. Chim. Acta, 161* (1989) 87.

6 A. Camus, N. Marsich and A. M. Manotti Lanfredi, unpublished results.

7 J. A. Schuerman, F. R. Fronczek and J. Selbin, *Inorg. Chim. Acta, 148* (1988) 177.

8 A. M. Manotti Lanfredi, A. Tiripicchio, A. Camus and N. Marsich, *J. Chem. Soc., Dalton Trans.*, (1989) 753.

9 Tang Kaluo, Jin Xianglin, Xie Yun and Tang Youqi, *Sci. Sin., Ser. B, 30* (1987) 1.

10 Tang Kaluo, Jin Xianglin, Xiao Qunong and Tang Youqi, *Jiego Huaxue (J. Struct. Chem.)*, *7* (1988) 159, and refs. therein.

11 A. Schuerman, F. R. Fronczek and J. Selbin, *Inorg. Chim. Acta, 160* (1989) 43.

12 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A, 39* (1983) 158.

13 F. Ugozzoli, *Comput. Chem., 11* (1987) 109.

14 G. M. Sheldrick, *SHELX76*, system of computing program, University of Cambridge, U.K., 1976.

15 *International Tables for X-ray Crystallography*, Vol. 4, Kynoch Press, Birmingham, 1974.

16 J. P. Fackler, Jr, J. A. Fetchin and D. C. Fries, *J. Am. Chem. Soc., 94* (1972) 7323.

17 Kaluo Tang, M. Aslam, E. Block, T. Nicholson and J. Zubieta, *Inorg. Chem., 26* (1987) 1488.

18 F. A. Cotton, L. R. Falvello, C. A. Murillo and G. Valle, *Z. Anorg. Allg. Chem., 540/541* (1986) 67.

19 M. J. Freeman, A. G. Orpen and I. D. Salter, *J. Chem. Soc., Dalton Trans.*, (1987) 1001.

20 G. Henkel, B. Krebs, P. Betz, H. Fietz and K. Saatkamp, *Angew. Chem., Int. Ed. Engl., 27* (1988) 1326.

21 G. Pellizer and A. Camus, unpublished results.

22 G. Pellizer, N. Marsich and A. Camus, *Inorg. Chim. Acta, 155* (1989) 167.