ELSEVIER

www.elsevier.com/locate/ica
Inorganica Chimica Acta 324 (2001) 162–172

Inorganica
Chimica Acta

Synthesis and crystal structure of some (2,2′-dipyridylamine)(carboxylato)(phenoxo)copper(II) complexes with rather unusual phenoxo ligands

Alessandro Facchinetti [a], Nazario Marsich [a], Annamaria Camus [a,*], Franco Ugozzoli [b], Chiara Massera [b], Anna Maria Manotti Lanfredi [b,*]

[a] *Dipartimento di Scienze Chimiche, Università degli Studi di Trieste, Via Giorgieri 1, 34127 Trieste, Italy*
[b] *Dipartimento di Chimica Generale e Inorganica, Chimica Analitica, Chimica Fisica, Università degli Studi di Parma, Centro di studio per la Strutturistica Diffrattometrica del CNR, Parco Area delle Scienze 17/A, 43100 Parma, Italy*

Received 8 May 2001; accepted 13 July 2001

Abstract

Some ternary Cu(dipyam)(OOCR)(OR) complexes (dipyam = 2,2′-dipyridylamine; $RCOO^-$ = acetate, benzoate, cmb (2-chloro-5-methylthio-benzoate), mta (methylthioacetate), mtn (2-methylthio-nicotinate); OR^- = pnp (*p*-nitrophenolate), dcp (2,6-dichlorophenolate), tcp (2,4,6-trichlorophenolate)) have been synthesized. Their IR spectra are included and the X-ray diffraction structure is given for the crystals of [Cu(dipyam)($OOCCH_3$)(dcp)] (**I**), [Cu(dipyam)(mta)(dcp)] (**II**), [Cu(dipyam)(mtn)(dcp)] (**III**) and [Cu(dipyam)(cmb)(tcp)] (**IV**). The copper coordination is square pyramidal in **I**, with a rather rare axial position of the phenolate ligand, while in **II** and **III** is distorted octahedral with equatorial phenolate and weak apical bonds (**II** Cl, S; **III** Cl, O). The copper coordination in **IV** can be better described as square planar, but with distortion toward a flattened tetrahedral geometry and with a rather long apical Cu–O distance, involving an oxygen of the carboxylate ion. The entrance of the phenolate in an axial or equatorial position is due to the geometry imposed to the complex by the auxiliary ligand. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Copper(II) 2,2′-dipyridylamine complexes; Carboxylates; Axial and equatorial phenolates; X-ray structures

---

1. Introduction

Copper(II) complexes with phenoxo ligands have attracted great interest in the last years for the study of copper enzymes. Numerous tetra- or pentadentate complexes with polydentate ligands, where the phenolate is coupled with nitrogen donors, have been proposed as intermediates in the reaction mechanism of tyrosinase [1] or as models for the fungal enzyme galactose oxidase (GO) [2]. In the tyrosinase–cresolase activity, a monophenol binds to the axial position of one of the two copper centers of the oxy-site prior to catalytic activation; in the GO in resting form, the copper(II) ion is square pyramidal, weakly bonded to a tyrosinate in the axial position and to another tyrosinate, two histidine residues and a water (pH 7) or an acetate (from buffer, pH 4.5) ligand in the equatorial sites [3]. Till now, among the models studied, the X-ray characterized mononuclear copper(II) complexes with exogenous phenolates are rare [1c,2a] and also the species where phenols [2m] or phenolates [4] coordinate in an axial position are few. Here we report on a series of ternary copper(II) complexes with 2,2′-dipyridylamine (dipyam) and carboxylates, in which the third ligand is just a phenolate. The crystal structure of some of these complexes has been determined and suggests that the introduction of the phenolate in an axial or equatorial position depends on the sterical characteristics of the carboxylate.

---

* Corresponding authors. Tel.: + 39-0521-90 5432; fax: + 39-0521-90 5556 (A.M.M.).
E-mail address: manotti@unipr.it (A.M. Manotti Lanfredi).

PII: S0020-1693(01)00571-0

2. Experimental

2.1. Reagents

The chemicals for the syntheses of the compounds were all of reagent grade and were used as purchased. The Cu(dipyam)(OOCR)Br complexes were obtained in yields $\geq 90\%$ by adding a small excess of the corresponding sodium carboxylates to a 2:1 water/ethanol solution of equimolecular amounts of $CuBr_2$ and dipyam. They are light green compounds, sparingly soluble in water and methanol and practically insoluble in other innocent solvents. The Cu(dipyam)-(OOCR)NO_3 complexes were prepared like reported in the literature for the acetate [5], using, however, the carboxylate in small excess instead of the indicated carboxylate/copper ratio = 2. Notwithstanding, in the case of cmb and mta, the complexes isolated did not contain the NO_3 group and were proved to be the Cu(dipyam)$(OOCR)_2$ species. The other nitrato derivatives were prepared with yields $\leq 70\%$; they are green–blue or deep green in color and are appreciably more soluble in water and methanol than the corresponding bromo species. Silver chlorophenolates of excellent purity were prepared as reported in the literature [6]. They are powders, from yellow to brown in color and are practically insoluble in all the common solvents. The potassium *p*-nitrophenolate was prepared in situ by treatment of the phenol with the stoichiometric amount of KOH in methanol.

2.2. Syntheses

2.2.1. Cu(dipyam)($OOCCH_3$)(pnp)

K(pnp) (2.9 mmol) in 20 ml of methanol was added to a hot solution of $[Cu(dipyam)(OOCCH_3)\text{-}\mu\text{-}NO_3]_n$ in the same solvent (1.00 g, 2.81 mmol in 100 ml of methanol). After 1 h of heating at reflux a light green precipitate formed was filtered off. The concentrated mother solution gave shining crystals of the title complex, which were rapidly washed with water to eliminate possible KNO_3 and then with methanol. Yield: 0.322 g, 26.5%. IR (KBr, cm^{-1}): 1658 m; 1599, 1578, 1560, 1538 s, br; 1478 s, br; 1438 s, br, shs; 1380 w; 1329 mw, 1286 s, br; 1243 mw, sh; 1160 m; 1107, 1102 ms; 1023, 1014, 991 w; 961 w; 910 w, sh; 853, sh, ms; 820 w; 768, 760 ms; 702, 684, 671 w; 645 ms, 620 w; 536, 524 w; 487 w; 432 w.

The product is insoluble in ether, acetone, acetonitrile, THF, ethyl acetate, nitromethane, DCE; is sparingly soluble (decomposes by heating) in pyridine, DMSO, DMF, hot water, methanol, and ethyl acetoacetate.

When the reaction was carried out in water, in the presence of a phenolate excess, the main product was the $[Cu(dipyam)(pnp)_2]$.

2.2.2. Cu(dipyam)($OOCC_6H_5$)(pnp)

A methanol solution of K(pnp) (0.17 g, 1.2 mmol) was added, under heating, to a methanol solution of Cu(dipyam)($OOCC_6H_5$)NO_3 (0.50 g, 1.2 mmol, 30 ml of solvent). After 1 h the green–black solution was filtered clear and left for slow evaporation in the air. A part from other products, which were removed by filtration, few big crystals of the required complex separated from the last part of the very concentrated mother liquor. They were recrystallized from hot ethanol. IR (Nujol, Hostaflon, cm^{-1}): 1652 m; 1597, 1585 ms; 1539 m, br; 1482 s; 1438 s; 1398 m; 1331 mw; 1281 m, br; 1239 w; 1162 m; 1106 mw; 1020, 1015 w; 857 mw; 767 m; 720 ms; 685 w; 643 w; 536 w; 470 w; 428 w; 350 w.

The product shows a small solubility in hot water, acetone and acetonitrile, while it is insoluble in ether, toluene, dichloroethane, THF.

2.2.3. Cu(dipyam)(cmb)(pnp)

K(pnp) (1 mmol) in 20 ml of methanol was added to a suspension of Cu(dipyam)(cmb)Br (0.52 g, 1 mmol) in 50 ml of the same solvent. A clear green–black solution was formed. When its volume was reduced to a half by evaporation and an equal volume of water was added, the title complex separated, in high yield, as a solid, which was filtered off and washed repeatedly with water. IR (KBr, cm^{-1}): 1653 m, br; 1579 s, 1551, 1532 ms; 1481 s; 1434, 1422 m; 1367 ms; 1330 m; 1286 s, br; 1166, 1155 m; 1106 m; 1035, 1025, 1012 w; 909, 892, 877 w; 855 mw; 800 w; 787, 764 m; 645 mw; 542, 534 w; 475 w; 434, 420 w.

The complex is insoluble in water, ether, acetone, ethylacetate, acetonitrile, chloroform and toluene; moderately soluble in hot methanol.

2.2.4. [Cu(dipyam)($OOCCH_3$)(dcp)] (**I**)

(i) Solid Ag(dcp) (0.135 g, 0.5 mmol) was added to a suspension of 0.19 g (0.5 mmol) of Cu-(dipyam)($OOCCH_3$)Br in 40 ml of methanol. The green starting complex disappeared and the color of the solution darkened, while AgBr was formed. After 1 h of stirring the mixture was filtered and the filtrate concentrated to about 20 ml. The first solid formed, $[Cu(dipyam)(dcp)_2]$, was filtered off and ethyl acetate was added to the filtrate. Crystals, suitable for X-ray diffraction, were obtained by partial slow evaporation of the filtrate. IR (Nujol, cm^{-1}): 1649 m, br; 1589 mw; 1570 w; 1536 m, br; 1296 mw, 1278 w; 1242 w, br; 1164 m; 1077 w, 1062 w; 1020 mw; 950 w; 913 w; 887, 882 w; 850 m; 770 s, 759 w; 737 s; 695 w, 679 w; 658 w; 620, 610 mw; 535 w; 425 mw; 364 w, br; 323 w, br.

In water the mixed complex slowly disproportionated to Cu(dipyam)$(OOCCH_3)_2$ and Cu(dipyam)$(dcp)_2$.

The product is insoluble in ether and acetone, decomposes by heating in water, acetonitrile, THF, toluene, chlorinated solvents, but is apparently well soluble in ethyl acetate, ethyl acetoacetate, nitromethane, DMF, DMSO.

(ii) A solution of [Cu(dipyam)(dcp)$_2$] (1.2 g, 2 mmol) in 50 ml of dichloroethane was treated with some drops of CH_3COOH (2 N) in the same solvent, till the starting brown color changed to green, and an equal volume of diethyl ether was added to the clear filtrate. The product, separated as a light brown powder after some days in a refrigerator, was filtered off, washed repeatedly with water and dried in vacuo.

2.2.5. *Cu(dipyam)(OOCC$_6$H$_5$)(dcp)*

(i) A method analogous to that of Section 2.2.2 was followed, obtaining also in this case a blackish solution, which became green after evaporation in the air. The first solid precipitated, Cu(dipyam)(dcp)$_2$, was filtered out. The mother liquor, concentrated near dryness, gave needles of the title compound. IR (KBr, cm^{-1}): 1654 m; 1600, 1587 m, 1561 m, 1533 mw, 1479 s; 1442 w, 1433 mw; 1377 m, br; 1283 mw; 1234 mw; 1156 m; 1066 w; 1022, 1014 mw; 847 m; 768 ms, br; 732 w, 715 m; 686 w; 538 w; 440, 428 w, br.

At room temperature the product is insoluble in water and ether, sparingly soluble in acetone, methanol and ethanol, well soluble in pyridine; in hot solvents it is slightly soluble also in toluene, ethyl acetate and acetonitrile.

(ii) Solid Ag(dcp) (0.090 g, 0.333 mmol) was added to 0.143 g (0.328 mmol) of Cu(dipyam)(OOCC$_6$H$_5$)Br in 50 ml of hot methanol. The reaction was immediate, with the formation of AgBr, which was filtered out after half an hour of moderate heating. A high concentration of the filtrate gave the complex as a powder.

2.2.6. *Cu(dipyam)(cmb)(dcp)*

A suspension of 0.144 g (0.279 mmol) of Cu(dipyam)(cmb)Br and 0.076 g (0.282 mmol) of Ag(dcp) in 60 ml of methanol was allowed to react under stirring and mild heating. When the starting reagents disappeared, the reaction mixture was filtered to eliminate the precipitated AgBr and the deep brown filtrate was left for evaporation. Black crystals (deep green laminar aggregates at microscope) deposited.

IR (KBr, cm^{-1}): 1658 m; 1600 w, 1588 m; 1565, 1535 m; 1486 s; 1452 s, 1430 m; 1388, 1366 m; 1302 w, 1285 w; 1238 mw: 1168, 1160 m; 1107 w; 1064 w, br; 1038, 1018 w; 814 sh, 804 mw; 770 ms; 740 mw, 725 sh; 634 w, br; 547, 532 w; 445, 426 w.

The product is insoluble in water, ether, acetone, ethylacetate; very little soluble in hot methanol and n-PrOH; moderately soluble in acetonitrile, benzene, chlorinated solvents, methanol. It could be recrystallized unchanged from dichloromethane/ether or pyridine/ether.

2.2.7. *[Cu(dipyam)(mta)(dcp)] (**II**)*

(i) Hot equimolecular solutions of K(dcp) (1 mmol in 5 ml of methanol) and Cu(dipyam)(mta)$NO_3 \cdot H_2O$ (0.43 g, 1 mmol, in 40 ml of methanol) were mixed and stirred for 90 min. Compound **II** was separated from the brown mother solution as a powder. Yield: 0.332 g, 66.1%. IR (KBr, cm^{-1}): 1653 m; 1594 s; 1578 s, sh; 1534 m; 1473 s, 1453 s, 1434 s, sh; 1370 m, br; 1301 mw; 1240 mw; 1169 w, 1158 m; 1070, 1054 w; 1024, 1015 w; 906, 892, 879 w; 852, 832 w; 771 s; 733 m; 650 w; 624 w; 534 w; 455 w; 430 w, sh.

The product is sparingly or not at all soluble in water, ether, acetonitrile, nitromethane; soluble in methanol, hot acetone, toluene, ethyl acetate and ethyl acetoacetate.

(ii) A suspension of [Cu(dipyam)(mta)Br] (0.126 g, 0.300 mmol) and Ag(dcp) (0.081 g, 0.300 mmol) in 50 ml of methanol was stirred for 1 h. The solid residue was filtered off and the crystals of **II** were formed by concentration of the filtrate.

2.2.8. *Cu(dipyam)(mtn)(dcp) (**III**)*

A hot methanol suspension (50 ml) of Cu(dipyam)(mtn)Br (0.48 g, 1 mmol) and Ag(dcp) (0.27 g, 1 mmol) was stirred for 2 h, giving a dark red solution and a solid mixture of AgBr and a green compound. The solid component, filtered off, was dried and then extracted with hot dichloromethane. The extracts were added to the mother liquor and gave, after evaporation and addition of ethylacetate, the product as a powder. IR (KBr, cm^{-1}): 1652 m, br; 1602, 1587 ms; 1570 w; 1546 w; 1532 mw; 1478 s, sh; 1432, sh, mw; 1397, 1382 w; 1351 mw; 1286 mw; 1234 mw; 1159 m, sh; 1124 w; 1071 m; 1013 mw; 881 w; 854 m; 763 ms, sh; 730 m; 648 w; 580 w; 537 w; 489 w; 425 mw.

The complex is insoluble in water, acetone, ethylacetate, methanol, ethanol, ether, acetonitrile, toluene; moderately soluble in hot dichloromethane, chloroform and DCE.

2.2.9. *[Cu(dipyam)(cmb)(tcp)] (**IV**)*

A yellow–orange dispersion of 0.30 g (0.986 mmol) of Ag(tcp) in 20 ml of methanol was added, under stirring and mild heating, to a green suspension of [Cu(dipyam)(cmb)Br] complex (0.50 g, 0.97 mmol) in 50 ml of the same solvent. The mother liquor changed immediately to a dark brown color and the reagents disappeared in a few minutes, with contemporaneous formation of a mixture of AgBr and a bluish solid. After half an hour the mixture was filtered and the filtrate reduced by heating to about a quarter of the starting volume. Needles, suitable for X-ray diffraction, were separated by resting at room temperature. Additional amount of product was obtained by extraction with methanol of the first solid residue. IR (KBr, cm^{-1}): 1659 m; 1600 w, 1588 m; 1569 mw; 1537 mw;

Table 1
Crystal data and structure refinement parameters for **I**–**IV**

	I	**II**	**III**	**IV**
Empirical formula	$C_{18}H_{15}Cl_2CuN_3O_3$	$C_{19}H_{17}Cl_2CuN_3O_3S$	$C_{23}H_{18}Cl_2CuN_4O_3S$	$C_{24}H_{17}Cl_4CuN_3O_3S$
Formula weight	455.79	501.87	564.93	632.84
Diffractometer	Siemens AED	CAD4	Philips PW1100	CAD4
Wavelength (Å)	0.71073 (Mo Kα)	1.54178 (Cu Kα)	0.71073 (Mo Kα)	1.54178 (Cu Kα)
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
Unit cell parameters [a]				
a (Å)	7.803(5)	10.386(5)	10.323(5)	16.504(4)
b (Å)	16.857(5)	13.581(5)	13.595(5)	7.471(2)
c (Å)	13.684(5)	15.232(5)	8.878(5)	21.389(4)
α (°)	90	90	104.24(2)	90
β (°)	94.66(2)	93.57(2)	98.00(2)	103.75(2)
γ (°)	90	90	88.86(2)	90
V (Å^3)	1794(1)	2144(1)	1196(1)	2562(1)
Z	4	4	2	4
D_{calc} (g cm^{-3})	1.688	1.555	1.569	1.641
F(000)	924	1020	574	1276
Linear absorption coefficient (mm^{-1})	1.54	1.39	1.26	6.089
2θ Range (°)	3.12, 24.05	1.96, 25.67	3.01, 22.01	4.26, 69.98
Reflections measured	2932	4184	3155	4933
Unique data/restraints/parameters	2808/1/252	4026/0/271	2927/1/315	4796/0/328
Observed reflections	1818	3055	2079	3311
Final R indices [b]	$R_1 = 0.0763$, $wR_2 = 0.2448$	$R_1 = 0.0804$, $wR_2 = 0.1987$	$R_1 = 0.0468$, $wR_2 = 0.1077$	$R_1 = 0.0521$, $wR_2 = 0.1435$
Goodness-of-fit	1.021	0.953	0.925	1.022
Highest peak, deepest hole in final difference map (e Å^{-3})	2.035 and -0.627	1.547 and -1.555	0.634 and -0.708	0.715 and -0.602

[a] Unit cell parameters were obtained by least-squares analysis of the setting angles of 30 reflections found in a random search on the reciprocal space.

[b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$. Goodness-of-fit $= [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where n is the number of reflections and p the number of parameters.

1487 s; 1459 s; 1434, 1427 m; 1388, 1369 m; 1311,1301 w; 1236 m; 1171,1161 mw; 1106 w; 877, 862 w; 808, 800, 793 mw; 767 ms, 756 m; 614 w, br; 544, 529 mw; 422 w.

The complex is moderately soluble in hot methanol, ethanol, acetone, dichloroethane and toluene.

2.3. Apparatus

IR spectra (4000–200 cm^{-1}) were registered on Perkin–Elmer 983G and System 2000 spectrometers, as KBr pellets or as Nujols and Hostaflon mulls for the Cu(dipyam)(OOCC$_6$H$_5$)(pnp) and [Cu(dipyam)-(OOCCH$_3$)(dcp)] complexes, which reacted with KBr. The data reported above for each complex are relative to the 2000–200 cm^{-1} region. A Digital Conductivity Meter B.E. 103 was used for conductivity measurements and a Knauer Vapor Pressure Osmometer for the determination of molecular weights.

2.4. X-ray data collection and structure determination of *I*–*IV*

The single-crystal X-ray diffraction experiments were undertaken at room temperature using Mo Kα or Cu Kα graphite monochromated radiations. The unit cell parameters were obtained by least-squares fit of 17 (**I**), 31 (**II**), 29 (**III**), 34 (**IV**) $I(\theta\chi\phi)_{hkl}$ reflections in the range: $7 \leq \theta \leq 10°$ (**I**), $10 \leq \theta \leq 18°$ (**II**), $30 \leq \theta \leq 35°$ (**III**), $30 \leq \theta \leq 43°$ (**IV**).

The crystal data and the most relevant experimental parameters used in the X-ray measurements and in the crystal structure analysis are reported in Table 1. The intensities were calculated from the analysis of the $\omega/2\theta$ diffraction profiles.

During the systematic data collection, one standard reflection monitored every 100, indicated no significant fluctuations. The intensities were corrected for Lorentz and polarization effects. In compound **IV** the intensities were corrected for absorption effects using ABSORB [7].

The four structures were solved by direct methods using SIR-92 [8] whose E-maps revealed almost all the non-hydrogen atoms of the complexes. The rest of the structures was located by successive cycles of Fourier ΔF maps and refined by full-matrix least-squares on F^2 with SHELXL-97 [9] using anisotropic atomic displacements for all non-hydrogen atoms. For each complex

$$\text{(A)}\quad \mathrm{Cu(dipyam)(OOCR)NO_3 + OR^- \xrightarrow[\text{EtOH}]{\Delta} Cu(dipyam)(OOCR)(OR) + NO_3^-}$$

$\mathrm{OR^-}$ = *p*-nitrophenolate

$$\text{(B)}\quad \mathrm{Cu(dipyam)(OOCR)Br + AgOR \xrightarrow[\text{MeOH}]{} Cu(dipyam)(OOCR)(OR) + AgBr\downarrow}$$

$\mathrm{OR^-}$ = 2,6-dichlorophenolate
2,4,6-trichlorophenolate

Scheme 1.

the hydrogen atoms were added to the corresponding C atoms in the 'riding' model and refined with isotropic atomic displacements, whereas the hydrogen atoms of the NH bridge in the dipyam were found in the ΔF map and then refined. No unusual trends were found in F_o^2 versus F_c^2 as a function of $(\sin\theta)/\lambda$, Miller indices, and F_o^2.

All the geometrical calculations were carried out by PARST-97 [10]. All the plots were obtained by the ORTEP program in the WinGX suite [11].

All the calculations were carried out on the DEC Alpha 250 workstation at the Centro di Studio per la Strutturistica Diffrattometrica of C.N.R., Parma.

3. Results and discussion

3.1. Synthesis of the complexes

The synthesis of the complexes is sketched in Scheme 1. Different approaches were chosen for the introduction of the *p*-nitrophenolates or the chlorosubstituted phenolates, the latter being used as silver salts.

For the preparation of the *p*-nitrophenolate derivatives (procedure A in Scheme 1) we employed the Cu(dipyam)(OOCR)NO_3 complexes, although more difficult to isolate than the corresponding bromo derivatives. We preferred them not only for their higher solubilities, but because the nitrate group is more easily substituted than the bromide by the *p*-nitrophenolate. In the solid state the nitrate derivatives are probably chain polymers, with the nitrate group bridging two adjacent copper atoms, as in the [Cu(dipyam)-($OOCCH_3$)NO_3]$_n$ [5] and [Cu(dipyam)(propionate)-NO_3]$_n$ complex [12]. In water or methanol, however, mononuclear complexes are formed and dissociate in turn, as suggested from molecular weight determinations (values that are the half of the formula weights are obtained) and conductivity measurements (1:1 electrolytes). The introduction of a phenolate as a third ligand requires the presence of strong bases: the triethylamine, which in the literature is the almost exclusive reagent employed for the deprotonation of the phenolic group in polydentate ligands, was found inadequate for this kind of reactions. The coordination of the phenolate is conditioned both by its activation through appropriate substituents and by the type of the carboxylate ligand. Among the complexes with *p*-nitrophenolate studied, only the cmb derivative was easily obtained, acetate and benzoate gave very low yields and the mta and mtn species could not be isolated from the mixtures obtained in the reactions. Except for Cu-(dipyam)(cmb)(pnp), the first product to precipitate is not the required ternary compound, but a pea-green complex of rough formula $C_{17}H_{16}CuN_4O_4$, which is a dimer with bridging methoxide groups [13].

If the anion to substitute is a halide (procedure **B** in Scheme 1), silver phenolates are suitable for a direct reaction. The Cu(dipyam)(OOCR)Br complexes were suspended in methanol and treated with a stoichiometric amount of AgOR. The parent complex dissolved immediately, with contemporaneous formation of the new phenoxo species and solid AgBr. In the two [Cu-(dipyam)(OOCR)X] complexes of which we know the structures, the [Cu(dipyam)($OOCCH_3$)Cl] [14] and [Cu(dipyam)(methacrylato)Br] [13], the halide occupies the apical position of a square pyramidal geometry and hence we expected the phenolate to occupy the axial coordination site. As can be seen from the structures **I**–**IV** reported below, this is true for the acetato species but not for the complexes with other tested carboxylates.

The analytical data and some of the physical characteristics of the complexes are shown in Table 2.

Usually Cu(dipyam)$(OOCR)_2$ and minor amounts of Cu(dipyam)$(OR)_2$ are by-products of the syntheses of the Cu(dipyam)(OOCR)(OR) ternary compounds. This implies that in solution the three species are in equilibrium with each other

$$2\mathrm{Cu(dipyam)(OOCR)(OR)} \rightleftarrows \mathrm{Cu(dipyam)(OOCR)_2} + \mathrm{Cu(dipyam)(OR)_2}$$

so that the recrystallization of the mixed compounds is difficult and the study of their properties in solution is complicated.

3.2. IR spectra

The IR spectra of all these complexes are very complicated, as can be seen in Section 2, where a lot of absorption bands are reported for each product, al-

Table 2
Elemental analyses and some physical characteristics of the isolated complexes

Complex	Color	% Found (calculated)					Dec. p. (°C)
		C	H	Cl	Cu	N	
Cu(dipyam)(OOCCH$_3$)(pnp)	dark green	49.6 (50.05)	3.7 (3.73)		14.6 (14.71)	12.7 (12.79)	225
Cu(dipyam)(OOCC$_6$H$_5$)(pnp)	dark green	56.1 (55.93)	3.6 (3.67)		12.7 (12.86)	11.3 (11.24)	213–214
Cu(dipyam)(cmb)(pnp)	green	50.2 (50.18)	3.3 (3.33)	5.9 (6.17)	11.0 (11.06)	9.5 (9.75)	227–228
Cu(dipyam)(OOCCH$_3$)(dcp)	brown	47.3 (47.43)	3.4 (3.32)	15.3 (15.56)	13.8 (13.94)	9.2 (9.22)	221–222
Cu(dipyam)(OOCC$_6$H$_5$)(dcp)	grey–green	52.6 (53.55)	3.2 (3.31)	14.5 (13.69)	12.1 (12.27)	8.0 (8.11)	220–222
Cu(dipyam)(cmb)(dcp)	green–black	47.8 (48.17)	3.1 (3.03)	18.5 (17.77)	10.1 (10.62)	6.7 (7.02)	220–221
Cu(dipyam)(mta)(dcp)	green	45.4 (45.47)	3.2 (3.42)	14.4 (14.13)	12.5 (12.66)	8.2 (8.37)	167
Cu(dipyam(mtn)(dcp)	green–black	49.0 (48.90)	3.3 (3.21)	12.1 (12.55)	10.9 (11.25)	9.7 (9.92)	224–225
Cu(dipyam)(cmb)(tcp)	brown–blue	45.5 (45.55)	2.7 (2.71)	23.1 (22.41)	9.8 (10.04)	6.6 (6.64)	204–206

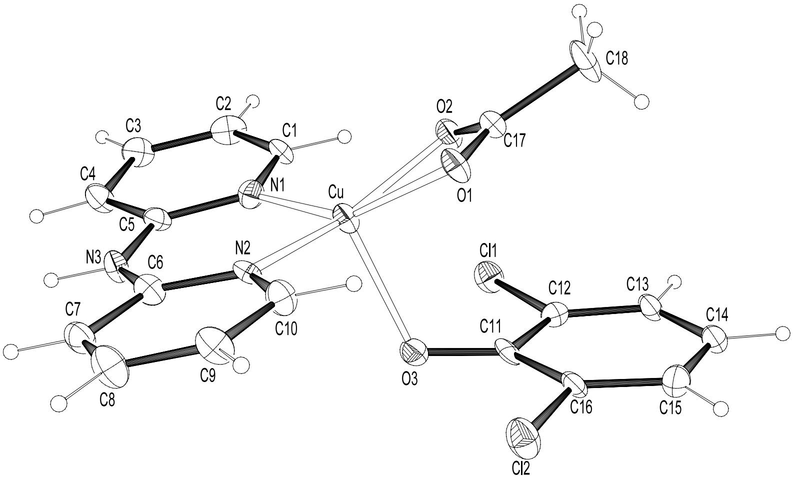

Fig. 1. ORTEP view (at 30% probability) of the molecular complex **I**, with the atomic numbering scheme.

though the minor ones are not considered. These spectra do not allow the attribution of the geometrical structure of the complexes, except for the expected chelation of the dipyam,[1] but provide, however, some useful suggestions. For example, the good correspondence between the spectral patterns of the Cu(dipyam)(cmb)(dcp) complex and its corresponding tcp derivative supports the expectation of a close geometry for these two compounds. Furthermore, while the patterns of the Cu(dipyam)(OOCR)(dcp) or tcp are similar to those of the Cu(dipyam)(OOCR)Br spectra (the bands of the phenolates obviously excluded), this is not true for the Cu(dipyam)(OOCR)(pnp) complexes.[2] The Cu(dipyam)(OOCC$_6$H$_5$)(pnp) spectrum rather resembles that of the Cu(dipyam)(OOCC$_6$H$_5$)(NO$_3$) and, hence, a catena structure for it cannot be excluded.

3.3. X-ray diffraction structures of I–IV

ORTEP views of complexes **I**–**IV**, are shown in Figs. 1–4, respectively. The selected bond distances and angles are given in Table 3. All the complexes are mononuclear with one chelating dipyam ligand and one metal O-bonded chloro-substituted phenolate.

In **I** the copper(II) ion exhibits a distorted square pyramidal arrangement of the N$_2$O$_3$ donor set with two mutually *cis* pyridyl N atoms from the bidentate dipyam (1.953(7)–1.972(8) Å), two mutually *cis* O atoms from a symmetrically bidentate acetate anion (1.999(6)–2.110(7) Å) and an axial O atom from a dcp ligand (2.164(6) Å). The equatorial atoms are roughly coplanar, with the Cu(II) out of 0.338(1) Å from the least-squares plane through the N$_2$O$_2$ donor set toward the vertex of the pyramid. The dipyam ligand is nearly planar with the two pyridine rings mutually bent of only 7.8(3)°. This complex, because of the correct se-

---

[1] The IR spectra of complexes with chelated dipyam are characterized by three medium absorption bands, of variable relative intensity, in the regions 1660–1630, 1600–1580, 1540–1520 cm^{-1}, a couple of bands of medium weak intensity at 1240–1230 and 1165–1150 cm^{-1}, a strong band at about 770 cm^{-1} and a second group of three weak or very weak bands around 540, 430 and 360 cm^{-1}.

[2] The spectra of complexes with pnp exhibit absorption peaks at about 1330 mw, 1288–1280 m, br and 1106 mw cm^{-1}, where both Cu(dipyam)(OOCR)Br and Cu(dipyam)(OOCR)$_2$ are free from absorption bands.

quence of atoms in the coordination sphere of copper, and the rather rare apical copper(II)–phenoxo bond, could be compared with the nuclear core of the galactose oxidase [3].

However, while the equatorial distances of **I** fall nearly in the range (1.94–2.27 Å) observed for the planar O_2N_2 donor set of the mononuclear GO, the Cu–O_{apical} distance is significantly shorter than the cor-

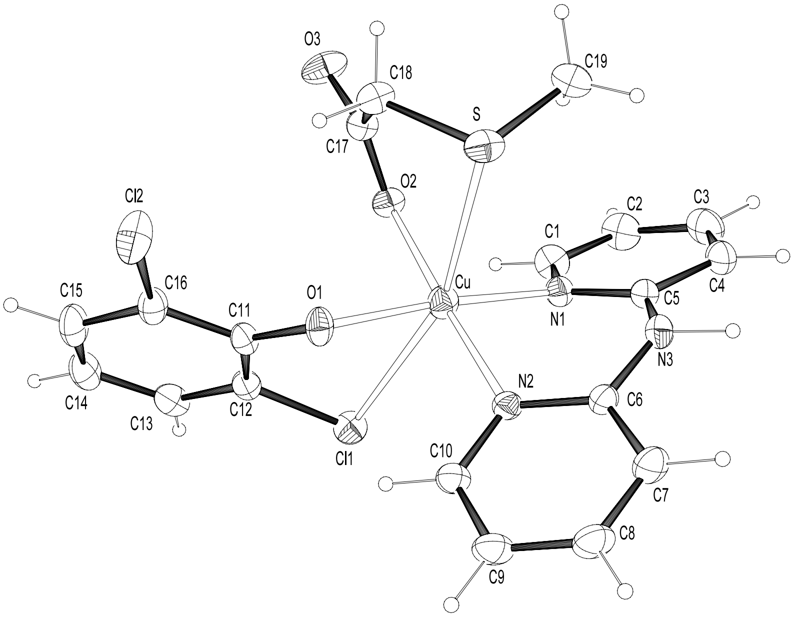

Fig. 2. ORTEP view (at 30% probability) of the molecular complex **II**, with the atomic numbering scheme.

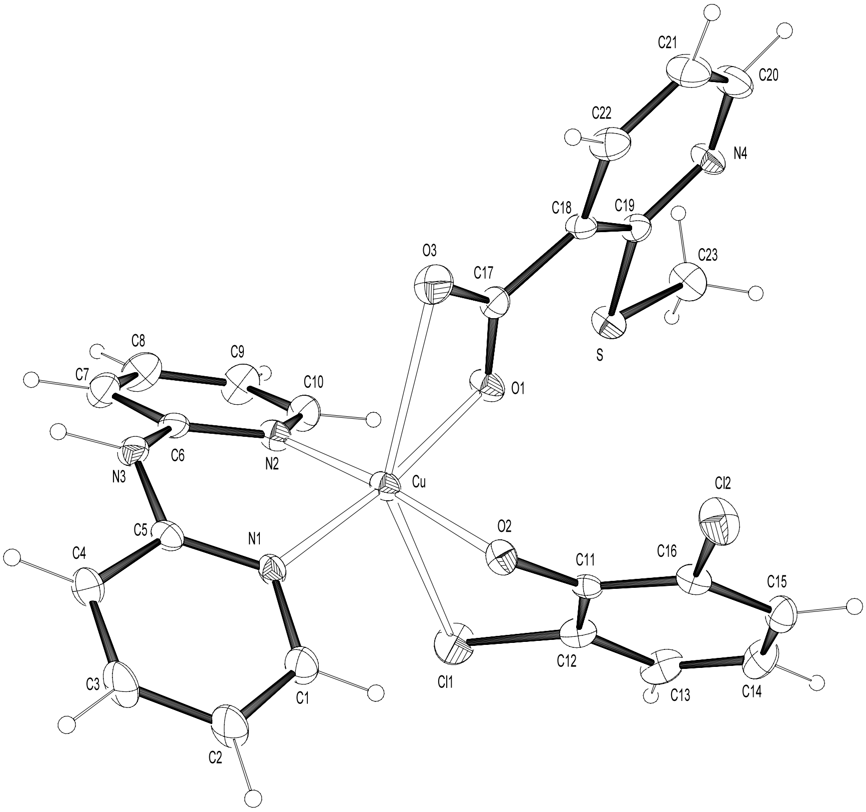

Fig. 3. ORTEP view (at 30% probability) of the molecular complex **III**, with the atomic numbering scheme.

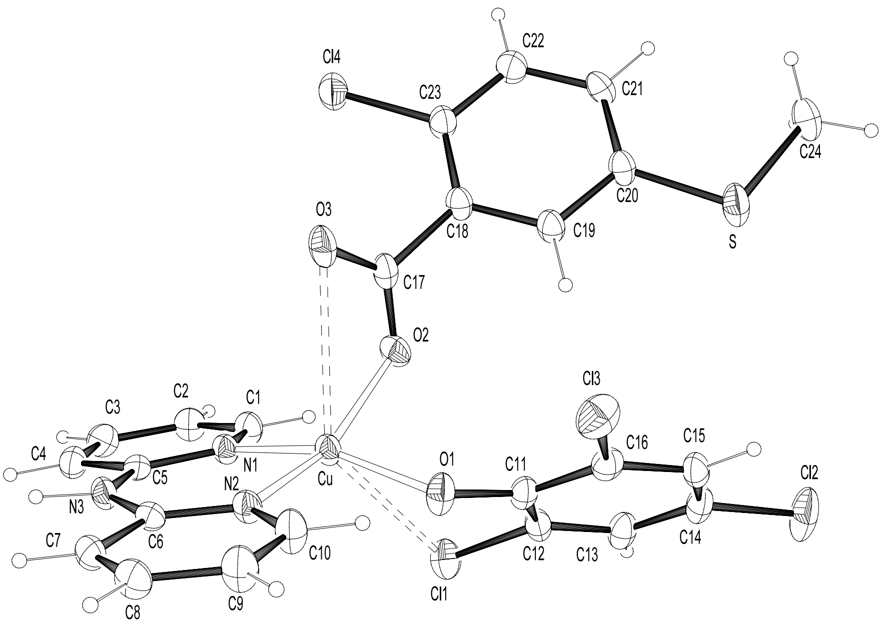

Fig. 4. ORTEP view (at 30% probability) of the molecular complex **IV**, with the atomic numbering scheme.

responding apical copper(II)–phenolic (tyrosine) oxygen bond (2.69 Å) in the enzyme. On the other hand, the Cu–phenoxo distance in **I** fits the short axial phenolate–copper(II) bond distances (2.176(5) Å [15] and 2.186(2) Å [3e]) found in mononuclear square pyramidal GO model complexes involving flexible tripodal ligands bearing phenolic arms. In the latter compounds the donor set of the basal plane are N_3O and N_4, respectively.

In **II** and **III** a distorted octahedral coordination is observed around the copper(II): four short in-plane bonds involve two mutually *cis* pyridyl N atoms from dipyam (1.995(4)–2.004(4) Å in **II** and 1.975(4)–1.997(4) Å in **III**), one O atom from equatorial dcp (1.939(3) Å in **II** and 1.910 (3) Å in **III**) and one O atom from carboxylate ligand (1.968(3) Å in **II** and 1.956(4) Å in **III**). The orientation of the dcp ligand, almost orthogonal to the least-squares plane through the N_2O_2 donor set (75.2(1) in **II** and 72.7(1)° in **III**), favors, in both compounds, a weak axial bond Cu···Cl (2.870(2) Å in **II** and 2.839(2) Å in **III**) with one *ortho*-chloro atom from dcp ligand. The different sterical characteristics of the mta and mtn ligands, however, allow the S atom of the less hindering mta (**II**) and the second O atom from the carboxylate group of the bulky mtn (**III**) to complete, with a relatively long interaction (Cu–S = 2.717(4) Å in **II** and Cu–O(3) = 2.721(4) Å in **III**), the coordination to that distorted octahedral. The dipyam ligands, in which the two pyridine rings are mutually bent by 26.4(2) (**II**) and 35.7(2)° (**III**), are preorganized for this type of coordination. The Cu–N and Cu–O equatorial distances in **II** are slightly longer than in complex **III** due to the steric effects of the methylene and methlythio neighboring groups of the mta ligand.

In complex **IV** the copper(II) coordination plane is formed by two mutually *cis* pyridine N atoms of the dipyam (1.982(4)–1.993(3) Å), by the O atom from the equatorial tcp (1.896(3) Å) and by one O atom from the cmb ligand (1.946(3) Å). The other atom of the carboxylate ligand forms a longer apical Cu–O bond (2.923(4) Å). One *ortho*-chloro atom of the equatorial phenolate anion interacts with the metal center at 3.089(2) Å, so that the copper(II) geometry can be described essentially as distorted square planar. The dipyam ligand is nearly planar with the two pyridine rings mutually bent of only 6.3(1)°. Complex **IV** has a structure similar to that of **II** and **III** mainly for the phenoxide O atom coordinated to copper(II) in one equatorial position. In **IV**, the chloro-substituted phenolate is tilted by 57.9(1)° with respect to the least-squares plane through the N_2O_2 donor set. The copper(II)–phenoxo distance and the equatorial copper(II)–carboxylate bond are the shortest among the series of the four complexes. This fact, together with the strongest displacement of the coordinated N and O atoms from the least-squares plane through the N_2O_2 equatorial set (N1 − 0.369(3), N2 0.453(4), O1 − 0.452(4) and O2 0.355(3) Å), supports a significant distortion of the geometry toward that flattened tetrahedral.

In **I**, **III** and **IV**, it is worth noting that the complexes are self-assembled in dimers, through cooperative N–H···O and C–H···Cl hydrogen bonds involving N–H and C–H groups from dipyam, and dcp O and Cl atoms in **I** (Fig. 5) [N3–H3N···O3′ = 2.79(1) Å, N3–H3N–O3′ = 148(7)°, C4–H4···Cl2′ = 3.63(1) Å, C4–H4–Cl2′ = 154(1)°, C7–H7···Cl1′ = 3.59(1) Å, C7–H7–Cl1′ = 155(1)°: primed atoms are in the equivalent position $1-x, -y, 2-z$], and through N–H···O hydrogen bonds between N–H dipyam groups and carboxylate O atoms involved in nearly axial interactions in **III** [N3–H3N···O3 ($-x, -y, -z$) 2.807(5) Å, N3–H3N–O3 ($-x, -y, -z$) = 174(3)° and in **IV** [N3–H3···O3 ($1-x, -y, -z$) 2.802(5) Å, N3–H3–O3 ($1-x, -y, -z$) = 174(1)°]. In **II** the N–H dipyam groups form hydrogen bonds with the carboxylate O atoms not interacting with the metal center [N3–H3N···O3 ($1-x, -1/2+y, 1/2-z$) 2.782(6) Å; N3–H3N–O3 ($1-x, -1/2+y, 1/2-z$) = 168(5)°], thus the complexes are linked in polymeric chains. The self-assembling of the mononuclear complexes by N–H···O bonds is partially maintained also in DCE solutions, where, for example, the cmb complexes with dichloro and trichlorophenolates, gave molecular weights higher than the theoretical ones (Cu(dipyam)(cmb)(dcp), FW 598; found 818; Cu(dipyam)(cmb)(tcp), FW 633, found 898). In methanol instead the Cu(dipyam)(OOCR)(OR) complexes show a significant dissociation, the molecular weights being about half of the formula weight and the conductivity around $50\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$.

Table 3
Selected bond lengths (Å) and bond angles (°) for the complexes [Cu(dipyam)($OOCCH_3$)(dcp)] (**I**), [Cu(dipyam)(mta)(dcp)] (**II**), [Cu(dipyam)(mtn)(dcp)] (**III**) and [Cu(dipyam)(cmb)(tcp)] (**IV**)

[Cu(dipyam)($OOCCH_3$)(dcp)] ***(I)***			
Cu–N1	1.972(8)	Cu–O2	1.999(6)
Cu–N2	1.953(7)	Cu–O3	2.164(6)
Cu–O1	2.110(7)		
N1–Cu–N2	93.9(3)	N2–Cu–O2	158.9(3)
N1–Cu–O2	97.5(3)	O3–Cu–N1	105.4(3)
O1–Cu–O2	63.6(3)	O3–Cu–N2	98.4(3)
O1–Cu–N2	98.5(3)	O3–Cu–O1	98.8(3)
N1–Cu–O1	150.8(3)	O3–Cu–O2	95.6(3)
[Cu(dipyam)(mta)(dcp)] ***(II)***			
Cu–N1	1.995(4)	Cu–O2	1.968(3)
Cu–N2	2.004(4)	Cu–S	2.717(2)
Cu–O1	1.939(3)	Cu–Cl1	2.870(2)
N1–Cu–N2	88.2(2)	O1–Cu–S	93.2(1)
N1–Cu–O2	90.3(2)	O2–Cu–S	80.0(1)
O1–Cu–O2	90.4(1)	N1–CuCl1	98.8(1)
O1–Cu–N2	91.4(2)	N2–Cu–Cl1	94.4(1)
N1–Cu–O1	172.6(2)	O1–Cu–Cl1	73.9(1)
N2–Cu–O2	177.2(1)	O2–Cu–Cl1	88.2(1)
N1–Cu–S	94.2(1)	Cl1–Cu–S	162.6(1)
N2–Cu–S	97.7(1)		
[Cu(dipyam)(mtn)(dcp)] ***(III)***			
Cu–N1	1.997(4)	Cu–O2	1.910(3)
Cu–N2	1.975(4)	Cu–O3	2.721(4)
Cu–O1	1.956(4)	Cu–Cl1	2.839(2)
N1–Cu–N2	89.5(2)	O1–Cu–O3	93.9(1)
N1–Cu–O2	91.7(2)	O2–Cu–O3	53.4(1)
O1–Cu–O2	89.1(2)	N1–CuCl1	99.6(1)
O1–Cu–N2	91.9(2)	N2–Cu–Cl1	94.9(1)
N1–Cu–O1	168.2(2)	O1–Cu–Cl1	92.0(1)
N2–Cu–O2	169.6(2)	O2–Cu–Cl1	74.7(1)
N1–Cu–O3	114.8(2)	Cl1–Cu–O3	144.2(1)
N2–Cu–O3	95.1(2)		
[Cu(dipyam)(cmb)(tcp)] ***(IV)***			
Cu–N1	1.982(4)	Cu–O2	1.946(3)
Cu–N2	1.993(3)	Cu–O3	2.923(4)
Cu–O1	1.896(3)	Cu–Cl1	3.089(2)
N1–Cu–N2	92.7(1)	O1–Cu–O3	105.5(1)
N1–Cu–O2	95.6(1)	O2–Cu–O3	49.8(1)
O1–Cu–O2	91.3(1)	N1–CuCl1	91.9(1)
O1–Cu–N2	90.3(1)	N2–Cu–Cl1	124.5(1)
N1–Cu–O1	158.0(1)	O1–Cu–Cl1	68.7(1)
N2–Cu–O2	153.4(1)	O2–Cu–Cl1	80.4(1)
N1–Cu–O3	94.9(1)	Cl1–Cu–O3	130.2(1)
N2–Cu–O3	104.4(1)		

4. Conclusions

Aromatic carboxylates of noticeable steric hindrance (complexes **III** and **IV**) gave distorted square planar geometries, in which the carboxylic group acts mainly as monodentate and enters in an equatorial position like the phenolate. However, both the structures could also be considered distorted octahedric, if the second oxygen of the carboxylate and one of the two chlorine atoms in the *ortho* position of the phenolate are judged at a bonding distance. On the other hand, when the carboxylate ion is small and without donor substituents, as for example, the acetate in complex **I**, the phenolate finds room in the apical position of a square based pyramidal geometry.

The first X-ray characterized complex with an axial metal–*O*-phenolate bond is that reported by Rajendran et al., with a tripodal tetradentate ligand, the (2-hydroxy-5-nitrobenzyl)bis(2-pyridylmethyl)amine and a chloride as second counter-ion [4]. The unusual site of coordination of the phenolate is attributed to its strong activating nitro group, which renders the phenolic arm the most electronegative of the ligand. As a consequence the phenolate is considered to occupy the axial position in agreement with the classic rule for a tetragonal based pyramid in main group chemistry [4]. This suggestion was rejected by Adam et al., who, studying a series of compounds with similar ligands, concluded that the position of the phenolate is decided by sterical factors [15,16].

Our results are in agreement with the point of view of the latter researchers. The substituents of the ligands can sometimes decide the geometry of the complex, bonding directly to the metal atom [2a, 17, see also our complex **II**].

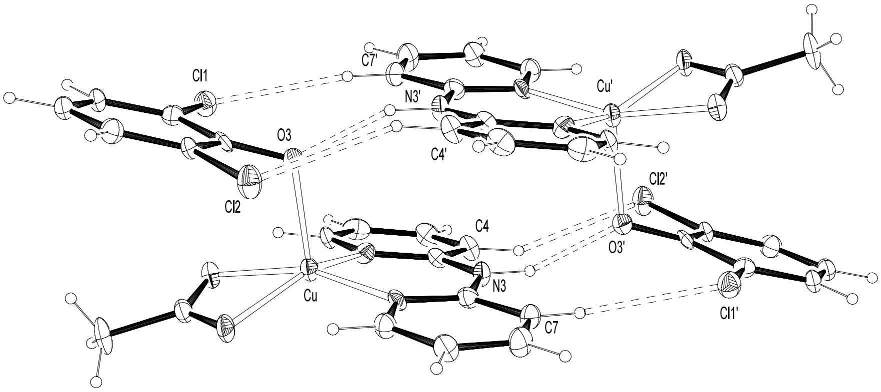

Fig. 5. ORTEP view (at 30% probability) of one of the centrosymmetric dimers present in **I**, showing the molecular complexes unusually self-assembled by three hydrogen bonds.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 162328, 162326, 162327, 162325 for compounds **I**–**IV**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the Italian MURST. We thank Mr. P. de Baseggio for running the IR spectra and Dr. E. Cebulec for the elemental analyses.

References

[1] (a) E.I. Solomon, U.M. Sundaram, T.E. Machonkin, Chem. Rev. (1996) 2563;
(b) W.B. Tolman, Acc. Chem. Res. 30 (1997) 227;
(c) K. Fujisawa, Y. Iwata, N. Kitajima, H. Higashimura, M. Kubota, Y. Miyashita, Y. Yamada, K. Okamoto, Y. Moro-oka, Chem. Lett. (1999) 739;
(d) A. Neves, L.M. Rossi, A. Horn Jr., I. Vencato, A.J. Bortoluzzi, C. Zucco, A.S. Mangrich, Inorg. Chem. Commun. 2 (1999) 334.

[2] (a) M.M. Whittaker, Y.Y. Chuang, J.W. Whittaker, J. Am. Chem. Soc. 115 (1993) 10029;
(b) M.M. Whittaker, W.R. Duncan, J.W. Whittaker, Inorg. Chem. 35 (1996) 382;
(c) J.A. Halfen, B.A. Jadzewski, S. Mahapatra, L.M. Berreau, E.C. Wilkinson, L. Que Jr., W.B. Tolman, J. Am. Chem. Soc. 119 (1997) 8217;
(d) A. Sokolowski, H. Leutbecher, T. Weyhermüller, R. Schnepf, E. Bothe, E. Bill, P. Hildebrandt, K. Wieghardt, JBIC 2 (1997) 444;
(e) E. Saint-Aman, S. Ménage, J.L. Pierre, E. Defrancq, G. Gellon, New J. Chem. (1998) 393;
(f) S. Ito, S. Nishino, H. Itoh, S. Ohba, Y. Nishida, Polyhedron 17 (1998) 1637;
(g) M.A. Halcrow, L.M.L. Chia, X. Liu, E.J.L. McInnes, L.J. Yellowlees, F.E. Mabbs, I.J. Scowen, M. McPartlin, J.E. Davies, J. Chem. Soc., Dalton Trans. (1999) 1753;
(h) P. Chauduri, M. Hess, J. Müller, K. Hildenbrand, E. Bill, T. Weyhermüller, K. Wieghardt, J. Am. Chem. Soc. 121 (1999) 9599;
(i) K. Yamato, T. Inada, M. Doe, A. Ichimura, T. Takui, Y. Kojima, T. Kikunaga, S. Nakamura, N. Yanagihara, T. Onaka, S. Yano, Bull. Chem. Soc. Jpn. 73 (2000) 903;
(j) Y. Shimazaki, S. Huth, A. Odani, O. Yamauchi, Angew. Chem., Int. Ed. Engl. 39 (2000) 1666;
(k) Y. Shimazaki, S. Huth, S. Hirota, O. Yamauchi, Bull. Chem. Soc. Jpn. 73 (2000) 1187;
(l) M. Taki, H. Kumei, S. Itoh, S. Fukuzumi, J. Inorg. Biochem. 78 (2000) 1;
(m) M. Taki, H. Kumei, S. Nagatomo, T. Kitagawa, S. Itoh, S. Fukuzumi, Inorg. Chim. Acta 300–302 (2000) 622;
(n) K. Yamato, T. Inada, M. Doe, A. Ichimura, T. Takui, Y. Kojima, T. Kikunaga, S. Nakamura, N. Yanagihara, T. Onaka, S. Yano, Bull. Chem. Soc. Jpn. 73 (2000) 903.

[3] (a) N. Itoh, S.E.V. Phillips, C. Stevens, Z.B. Ogel, M.J. McPherson, J.N. Keen, K.D.S. Yadav, P.F. Knowles, Nature 350 (1991) 87;
(b) N. Itoh, S.E.V. Phillips, K.D.S. Yadav, P.F. Knowles, J. Mol. Biol. 238 (1994) 794;
(c) H. Masuda, A. Odani, O. Yamauchi, Inorg. Chem. 28 (1989) 624;
(d) E.H. Alilou, E. Amadei, M. Giorgi, M. Pierrot, M. Reglier, J. Chem. Soc., Dalton Trans. (1993) 549;
(e) M. Yadyanathan, R. Viswanathan, M. Palaniandavar, T. Balasubramanian, P. Prabhaharan, T.P. Muthiah, Inorg. Chem. 37 (1998) 6418;
(f) P. Bandyopadhyay, P. Gosh, P.K. Bharadwaj, Indian J. Chem., A 37 (1998) 639.

[4] (a) U. Rajendran, R. Viswanathan, M. Palaniandavar, M. Lakshminarayanan, J. Chem. Soc., Dalton Trans. (1992) 3563;
(b) U. Rajendran, R. Viswanathan, M. Palaniandavar, M. Lakshminarayanan, J. Chem. Soc., Dalton Trans. (1994) 1219.

[5] S. Aduldecha, B. Hathaway, Acta Crystallogr., Sect. C 47 (1991) 84.

[6] W.H. Hunter, A.O. Olsen, E.A. Daniels, J. Am. Chem. Soc. 38 (1916) 1761.

[7] F. Ugozzoli, Comput. Chem. 11 (1987) 109 (ABSORB).

[8] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidori, J. Appl. Crystallogr. 27 (1994) 435 (SIR-92).

[9] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997, http://shelx.uni-ac.gwdg.de/shelx/index.html.

[10] M. Nardelli, J. Appl. Crystallogr. 28 (1995) 659 (PARST-97, updated version of PARST-95).

[11] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837 (WinGX).

[12] S. Youngme, C. Pakawatchai, H.K. Fun, Acta Crystallogr., Sect. C 54 (1998) 451.

[13] A.M. Manotti Lanfredi, F. Ugozzoli, A. Camus, unpublished results.

[14] F. Ugozzoli, A.M. Manotti Lanfredi, N. Marsich, A. Camus, Inorg. Chim. Acta 256 (1997) 1.

[15] H. Adams, N.A. Bailey, I.K. Campbell, D.E. Fenton, Q. He, J. Chem. Soc., Dalton Trans. (1996) 2233.

[16] H. Adams, N.A. Bailey, C.O. Rodriguez de Barbarin, D.E. Fenton, Q. He, J. Chem. Soc., Dalton Trans. (1995) 2323.

[17] S. Itoh, S. Takayama, R. Arakawa, A. Furuta, M. Komatsu, A. Ishida, S. Takamuku, S. Fukuzumi, Inorg. Chem. 36 (1997) 1407.