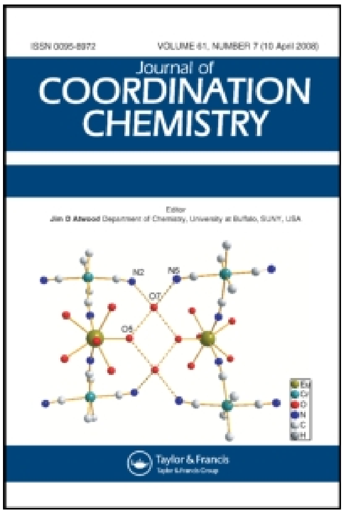


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Structural Relationships Afforded by the Coordination of 2,2'-Bipyridine to the (Iminodiacetato)Copper(II) Chelate: Synthesis, Structure and Properties of (2,2'-Bipyridine) (*N*-(2-Hydroxyethyl)Iminodiacetato) Copper(II)Tetrahydrate

I. S. dela Cueva-Torregrosa[a]; J. M. González-Pérez[a]; A. G. Sicilia-zafra[a]; E. Bugella-altamirano[a]; J. Niclós-Gutiérreza[a]; A. Castinteiras-Campos[b]
[a] Department of Inorganic Chemistry, Faculty of Pharmacy, University of Granada, Granada, Spain [b] Department of Inorganic Chemistry, Faculty of Pharmacy, University of Santiago de Compostela, Spain

To cite this Article Cueva-Torregrosa, I. S. dela , González-Pérez, J. M. , Sicilia-zafra, A. G. , Bugella-altamirano, E. , Niclós-Gutiérreza, J. and Castinteiras-Campos, A.(2000) 'Structural Relationships Afforded by the Coordination of 2,2'-Bipyridine to the (Iminodiacetato)Copper(II) Chelate: Synthesis, Structure and Properties of (2,2'-Bipyridine) (*N*-(2-Hydroxyethyl)Iminodiacetato) Copper(II)Tetrahydrate', Journal of Coordination Chemistry, 51: 2, 235 — 251

To link to this Article: DOI: 10.1080/00958970008055130

URL: http://dx.doi.org/10.1080/00958970008055130

J. Coord. Chem., 2000, Vol. 51, pp. 235–251
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

STRUCTURAL RELATIONSHIPS AFFORDED BY THE COORDINATION OF 2,2′-BIPYRIDINE TO THE (IMINODIACETATO)COPPER(II) CHELATE: SYNTHESIS, STRUCTURE AND PROPERTIES OF (2,2′-BIPYRIDINE) (*N*-(2-HYDROXYETHYL)IMINODIACETATO) COPPER(II)TETRAHYDRATE

I.S. DE LA CUEVA-TORREGROSA[a], J.M. GONZÁLEZ-PÉREZ[a],
A.G. SICILIA-ZAFRA[a], E. BUGELLA-ALTAMIRANO[a],
J. NICLÓS-GUTIÉRREZ[a,*] and A. CASTIÑEIRAS-CAMPOS[b]

[a]*Department of Inorganic Chemistry, Faculty of Pharmacy, University of Granada,*
E-18071 Granada, Spain; [b]*Department of Inorganic Chemistry,*
Faculty of Pharmacy, University of Santiago de Compostela,
E-15706 Santiago de Compostela, Spain

(Received 12 October 1999)

The stoichiometric reaction of copper(II) hydroxycarbonate, *N*-(2-hydroxyethyl)iminodiacetic acid [H_2heida=$HOCH_2CH_2N(CH_2CO_2H)_2$)] and 2,2′-bipyridine (bipy) in water yields crystalline (2,2′-bipyridine)(*N*-(2-hydroxyethyl)iminodiacetato)copper(II) tetrahydrate, [Cu(heida)-(bipy)]·$4H_2O$ (compound I). This was studied by TG analysis (with FT-IR study of evolved gases), IR, electronic and ESR spectra, magnetic susceptibility data and single crystal X-ray diffraction methods. The compound crystallises in the triclinic system, space group $P1$, $a = 7.011(2)$, $b = 12.586(3)$, $c = 13.052(3)$ Å, $\alpha = 62.14(1)$, $\beta = 80.51(2)$, $\gamma = 77.09(2)°$, $Z = 2$, final $R_1 = 0.051$ for 3900 independent reflections. The Cu(II) atom exhibits an asymmetric, elongated, octahedral coordination (type $4+1+1$), and bipy acts as an *N,N*-bidentate ligand supplying two among the four closest donor atoms of the metal (Cu–N bond lengths of 1.994(2) and 2.053(2) Å); heida plays an *N,O,O′,O″*-tetradentate chelating role (bond lengths Cu–N = 2.075(2), Cu–O(carboxyl) = 1.958(2), Cu–O′(carboxyl) = 2.337(2) and Cu–O″(hydroxyl) = 2.459(2) Å). The effective bidentate chelation of bipy imposes *fac*-chelation to the iminodiacetate moiety of heida in I, as previously reported in mixed-ligand complexes having a 1 : 1 : 2 Cu(II)/IDA/*N*(heterocyclic) or a 1/1/(1 + 1) Cu/IDA/(*N*-heterocyclic + *N*-aliphatic) donor ratio. The tetradentate role of heida in I reveals its noticeable conformational flexibility. The crystal

---

[*] Corresponding author.

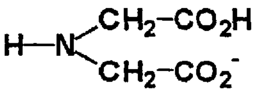
features a hydrogen bond network forming supra-molecular chains extending along the *a* axis. These are linked by two symmetry-related hydrogen bonds of the type O(hydroxyl)-H $\cdots$ O^i(carboxyl) between two adjacent complex units (symmetry code $i = -x, -y+1, -z+1$), related to each other by an inversion centre.

Keywords: *N*-(2-hydroxyethyl)iminodiacetic acid; *N*-(β-hydroxyethyl)-iminodiacetic acid; (2,2′-bipyridine)(*N*-(β-hydroxyethyl)-iminodiacetato)copper(II) tetrahydrate; crystal structure; properties; thermal stability

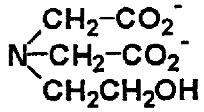
INTRODUCTION

The crystal structure of diaqua(iminodiacetato)copper(II) ([Cu(IDA)-($H_2O)_2$]) was reported and re-determined by independent groups.[1-3] In this complex the IDA ligand adopts a *fac*-chelating conformation and the copper(II) atom can complete its coordination polyhedron with two aqua ligands plus an *O*-carboxylate donor from an adjacent IDA ligand. This compound is indeed a mixed-ligand complex which can serve as starting reagent for the synthesis of others providing that the aqua ligand could be replaced by more basic ones. In this connection such ternary complexes can be looked upon as reference compounds for a large variety of mixed-ligand Cu(II) complexes having IDA and one *N*-heterocyclic donor ligand (or a closely related one).[3-23] These compounds include a primary chelating ligand such as IDA itself[3-5,7,9-12,14-17,21-23] or an *N*-substituted-IDA[6,8,11-14,18] or *C*-substituted-IDA[10] derivative. In addition, they include a large variety of *N*-heterocyclic donors. For example, imidazole (Him)[6,7,10,11,14,15,21] or an Him derivative,[3,8,9,11-14,21] 2,2′-bipyridine (2,2′-bipy or simply bipy),[16,18] 4,4′-bipyridine (4,4′-bipy),[4] 1,4-pyrazine,[5] 1,10-phenanthroline (phen),[19,20] α-picolinamide[22] or terpyridine (terpy),[23] are examples.

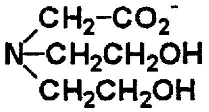
Recent structural studies on the abovementioned mixed-ligand copper(II) complexes have afforded several interesting structural correlations. For example, in compounds having equimolar Cu(II)/IDA/*N*-heterocyclic donor ratios[3-14] the Cu(II) exhibits a distorted square base pyramidal coordination (type 4 + 1) or more rarely an octahedral one (type 4 + 2 or 4 + 1 + 1). The Cu–*N*(heterocyclic) bond distance falls in the range 1.93–1.96(1) Å, the bond length Cu–*N*(IDA or IDA-derivative) is 1.99–2.01(1) Å, and the IDA or IDA-like ligand acts as terdentate exhibiting *mer*-chelation (giving two nearly coplanar five-membered chelate rings). In clear contrast diaqua(iminodiacetato)copper(II) itself[1-3] and all known mixed-ligand complexes having a 1 : 1 : 2 Cu/IDA/*N*-heterocyclic donor ratio[15,16,18-20] or a 1/1/(1 + 1) Cu/IDA/(*N*-heterocyclic + *N*-aliphatic) donor ratio[17,21] show an elongated octahedral Cu(II) coordination (type 4 + 2 or 4 + 1 + 1) or more rarely distorted square pyramidal coordination (type 4 + 1), and the IDA ligand with a *fac*-terdentate chelating role (giving two nearly perpendicular five-membered chelate rings in such cases). Consequently the conformation of IDA or IDA-derivatives bonding to copper(II) can be modulated by the appropriate choice of secondary ligands. A remarkable observation arises from these studies concerning the flexibility of the primary ligands and closely related ones. In this broad context, we became interested to prepare and study analogous compounds with *N*-substituted-IDA ligands. A particular IDA-derivative set includes those ligands having a chelatable side chain as *C*- or *N*-substituent. For example, there is structural evidence that the *N*-2-hydroxyethyl-iminodiacetate(2−) ion (heida)[18,19,24–41] and *N*,*N*-bis(hydroxyethyl)glycinate(1−) ion (bicine(1−) anion[42–49] display certain conformational flexibility in metal chelates. Such flexibility seems enhanced in copper(II) complexes[18,19,33,45–49] because of its capacity to give severely distorted environments.



IDA (2-) ion



heida (2-) ion



bicine (2-) ion

As a part of our research program[3,6–15,17,18,20–22,33] we decided to synthesise and study a copper(II) complex having heida as primary ligand and bipy as a secondary one. In the course of our work[18,33] we became aware of a structural report on the closely related compound (1,10-phenanthroline)(*N*-(2-hydroxyethyl)iminodiacetate)copper(II) heptahydrate, [Cu(heida)(phen)]·$7H_2O$.[19] The results reported here are discussed, taking into account this closely related contribution.

EXPERIMENTAL

Synthesis of the Title Compound

(2,2′-Bipyridine)(*N*-(2-hydroxyethyl)iminodiacetato)copper(II) tetrahydrate, [Cu(heida)(bipy)]·$4H_2O$ (compound I) was obtained by reaction of

$Cu_2CO_3(OH)_2$ (321 mg, 1.41 mmol), H_2heida acid (500 mg, 2.82 mmol, Sigma) and bipy (440 mg, 2.82 mmol, Aldrich) in water (100 cm^3) in a Kitasato flask, heating ($t < 50$°C) and stirring under reduced pressure (to remove the CO_2 by-product). The resulting blue solution was stirred and heated at 60°C for half an hour. Then it was left to cool at room temperature and slowly filtered to remove any insoluble by-product (a small amount of CuO). By slow evaporation of the clear solution at room temperature, well-shaped crystals of the desired product appeared and were filtered off and air dried. The blue compound is stable at room temperature without apparent water loss. It can be recrystallised by evaporation at room temperature from its solution in hot water (60°C). Yield: 85%. *Anal.* calcd. for $C_{16}H_{25}CuN_3O_9$(%): C, 41.16; H, 5.40; N, 9.00; Cu, 13.61. Found: C, 41.12; H, 5.38; N, 9.07; Cu, 13.53 (complexometry[50]). Alternatively, compound **I** can be obtained by dissolving in water equimolar amounts of aqua(*N*-hydroxyethyl)iminodiacetato)copper(II) monohydrate, $[Cu(heida)(H_2O)]\cdot H_2O$, compound **II**, and bipy, and evaporating the resulting solution at room temperature. This latter compound can be prepared as in the literature[33] or as above described for compound **I** but with addition of bipy. These syntheses will be preferred if an homogeneous sample of copper(II) hydroxycarbonate is not available.

X-ray Data Collection and Reduction, Structure Solution and Refinement

A blue prismatic crystal of $[Cu(heida)(bipy)]\cdot 4H_2O$ was mounted on a glass fibre and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data from 25 reflections in the range $6.46 < \theta < 13.056$ using an Enraf Nonius CAD4-automatic diffractometer.[51] Data were collected at 293(2) K using MoKα ($\lambda = 1.54184$ Å) radiation and the ω-scan technique, and were corrected for Lorentz and polarisation effects.[42] A semi-empirical absorption correction (Psi scan) was made.[52] The structure was solved by direct methods[53] which revealed the positions of all non-hydrogen atoms, and refined on F^2 by a full-matrix least-squares procedures using anisotropic displacement parameters.[54] All hydrogen atoms were located from difference maps and were refined isotropically. Atomic scattering factors were taken from *International Tables for X-ray Crystallography.*[55] Molecular graphics were obtained from ZORTEP[56] and SCHAKAL.[57] A summary of the crystal data, experimental details and refinement results are listed in Table I. Atomic coordinates of non-hydrogen atoms are given in Table II. Full lists of crystallographic data are available from the authors upon request.

TABLE I Crystal data and structure refinement for compound I, [Cu(heida)(bipy)] · $4H_2O$

Empirical formula	$C_{16}H_{25}CuN_3O_9$
Formula weight	466.93
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, $P1$
Unit cell dimensions	$a = 7.011(2)$ Å $b = 12.586(3)$ Å $c = 13.052(3)$ Å $\alpha = 62.14(2)°$ $\beta = 80.51(2)°$ $\gamma = 77.09(2)°$
Volume	990.1(4)A^3
Z, Calculated density	2, 1.566 Mg m^{-3}
Absorption coefficient	1.158 mm^{-1}
$F(000)$	486
Crystal size	0.40 × 0.10 × 0.10 mm
θ range for data collection	3.09–26.05
Index ranges	$-1 \leq h \leq 8, -15 \leq k \leq 15, -16 \leq l \leq 16$
Reflections collected/unique	4904/3900 [$R(int) = 0.0207$]
Completeness to $2\theta = 74.29$	98.4%
Absorption correction	semi-empirical, Psi scan
Max. and min. transmission	1.000 and 0.954
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3900/0/362
Goodness-of-fit on F^2	1:050
Final R indices [$I > 2\text{sigma}(I)$]	$R1 = 0.033$, $wR2 = 0.080$
R indices (all data)	$R1 = 0.051$, $wR2 = 0.086$
Largest diff. peak and hole	0.717 and −0.662 e $Å^{-3}$

Physical Measurements

Infrared spectra were obtained by the KBr disc technique on a Beckman IR 4260 instrument. TG (pyrolysis) of studied compounds and analysis of evolved gases were recorded (295–875 K) in air flow (100 cm^3/min) using a Shimazu Thermobalance TGA-DTG-50H coupled with an IR-FT Nicolet Magma 550 (and Fisons Thermolab mass spectrometer). Electronic (reflectance) spectra (175–3300 nm) were obtained using a Cary 5E spectrophotometer. RSE spectra of polycrystalline samples were recorded without magnetic dilution on a Bruker ESP 300E (X band) spectrophotometer at room temperature. Magnetic susceptibility was measured at the temperature range 80–300 K using a Manics DM magnetometer. The susceptometer was calibrated with mercury tetrakis(thiocyanato)-cobaltate(II). Corrections for the diamagnetism were estimated from Pascal constants.[58] Experimental susceptibilities were also corrected for temperature-independent paramagnetism.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for compound **I**, [Cu(heida)(bipy)] $\cdot$ $4H_2O$; *U*(*eq*) is defined as one third of the trace of the orthogonalised U_{ij} tensor

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
Cu(1)	2299(1)	3126(1)	3947(1)	32(1)
O(11)	5065(3)	3170(2)	2663(2)	43(1)
O(12)	5483(3)	3187(2)	926(2)	53(1)
O(21)	2404(3)	4503(2)	4237(2)	43(1)
O(22)	1904(3)	6520(2)	3461(2)	52(1)
O(31)	−1265(3)	3558(2)	4356(2)	45(1)
N(1)	1385(3)	4463(2)	2339(2)	31(1)
N(41)	2986(3)	1970(2)	5569(2)	37(1)
N(51)	2061(3)	1511(2)	3985(2)	32(1)
C(11)	2475(4)	4208(2)	1378(2)	35(1)
C(12)	4513(4)	3462(2)	1692(2)	36(1)
C(21)	1884(5)	5596(2)	2237(2)	40(1)
C(22)	2046(4)	5551(2)	3399(2)	38(1)
C(31)	−768(4)	4581(2)	2306(2)	39(1)
C(32)	−1899(5)	4650(3)	3371(2)	44(1)
C(41)	3378(5)	2295(3)	6339(2)	50(1)
C(42)	3649(5)	1461(4)	7487(3)	62(1)
C(43)	3544(5)	271(3)	7839(3)	59(1)
C(44)	3182(4)	−86(3)	7051(2)	49(1)
C(45)	2899(3)	790(2)	5917(2)	35(1)
C(46)	2502(3)	520(2)	4995(2)	33(1)
C(47)	2564(4)	−655(2)	5142(2)	41(1)
C(48)	2162(4)	−813(2)	4229(3)	45(1)
C(49)	1686(4)	198(3)	3203(3)	43(1)
C(50)	1647(4)	1337(2)	3110(2)	38(1)
O(1)	1911(5)	8553(2)	1299(2)	59(1)
O(2)	−1232(4)	8930(2)	−58(2)	66(1)
O(3)	536(4)	7134(2)	9232(2)	69(1)
O(4)	4539(5)	2356(3)	9522(3)	75(1)

RESULTS AND DISCUSSION

Bond lengths and angles of non-hydrogen atoms and hydrogen bonding data of compound **I** are listed in Table III. Figure 1 shows a plot of the complex molecule in **I** with the labelling of the atoms. This new compound consists of mononuclear [Cu(heida)(bipy)] units and non-bonded water molecules. The two heterocyclic nitrogen atoms N(41) and N(51) of the bipy ligand, and the atoms N(1, amino), O(11, carboxylato), O(21, carboxylato) and O(31, hydroxyl) of the heida ligand define an asymmetrically elongated coordination polyhedron to copper(II) (type 4 + 1 + 1). These three nitrogen atoms and O(21) are the four closest donors. Copper(II) is displaced 0.086(1) Å toward O(11). The *trans*-pair of donor atoms N(1) and N(41) are displaced 0.008(1) Å in the same sense as the metal atom, whereas N(51) and O(21) atoms are similarly moved (0.007(1) Å) but in the opposite sense.

TABLE III Selected bond lengths (Å) and angles (deg.) for compound **I**, [Cu(heida)-(bipy)]·$4H_2O$

Copper(II) environments			
Cu(1)–O(21)	1.9580(18)	O(21)–Cu(1)–N(41)	90.10(8)
Cu(1)–N(41)	1.994(2)	O(21)–Cu(1)–N(51)	168.83(7)
Cu(1)–N(51)	2.053(2)	N(41)–Cu(1)–N(51)	79.91(9)
Cu(1)–N(1)	2.075(2)	O(21)–Cu(1)–N(1)	84.53(7)
Cu(1)–O(11)	2.3368(19)	N(41)–Cu(1)–N(1)	173.20(8)
Cu(1)–O(31)	2.459(2)	N(51)–Cu(1)–N(1)	105.04(8)
Cu(1)–Cu(1)#1	6.5277(17)	O(21)–Cu(1)–O(11)	101.22(8)
Cu(1)–Cu(1)#2	7.0114(18)	N(41)–Cu(1)–O(11)	109.83(8)
Cu(1)–Cu(1)#3	7.0114(18)	N(51)–Cu(1)–O(11)	86.99(7)
		N(1)–Cu(1)–O(11)	75.41(7)
		O(21)–Cu(1)–O(31)	85.46(8)
		N(41)–Cu(1)–O(31)	97.59(8)
		N(51)–Cu(1)–O(31)	90.88(8)
		N(1)–Cu(1)–O(31)	77.87(8)
		O(11)–Cu(1)–O(31)	151.63(7)
Heida ligand			
O(11)–C(12)	1.247(3)	G(21)–N(1)–Cu(1)	104.54(15)
O(12)–C(12)	1.254(3)	C(11)–N(1)–Cu(1)	111.52(14)
O(21)–C(22)	1.262(3)	C(31)–N(1)–Cu(1)	110.20(15)
O(22)–C(22)	1.241(3)	N(1)–C(11)–C(12)	112.4(2)
O(31)–C(32)	1.416(3)	O(11)–C(12)–O(12)	125.9(3)
N(1)–C(21)	1.485(3)	O(11)–C(12)–C(11)	115.3(2)
N(1)–C(31)	1.489(3)	N(1)–C(21)–C(22)	118.8(2)
N(1)–C(11)	1.487(3)	O(12)–C(12)–C(11)	113.3(2)
C(11)–C(12)	1.525(4)	O(22)–C(22)–O(21)	124.5(2)
C(21)–C(22)	1.513(3)	O(22)–C(22)–C(21)	119.1(2)
C(31)–C(32)	1.513(4)	O(21)–C(22)–C(21)	116.3(2)
		N(1)–C(31)–C(32)	112.1(2)
		O(31)–C(32)–C(31)	108.0(2)
		C(12)–O(11)–Cu(1)	108.60(16)
		C(22)–O(21)–Cu(1)	116.33(16)
		C(32)–O(31)–H(310)	116(3)
		C(21)–N(1)–C(11)	108.76(19)
		C(21)–N(1)–C(31)	110.8(2)
		C(11)–N(1)–C(31)	110.80(19)
Bipy ligand			
N(41)–C(41)	1.333(4)	C(41)–N(41)–C(45)	118.8(2)
N(41)–C(45)	1.348(3)	C(41)–N(41)–Cu(1)	124.83(19)
N(51)–C(50)	1.344(3)	C(45)–N(41)–Cu(1)	116.22(17)
N(51)–C(46)	1.347(3)	C(50)–N(51)–C(46)	117.9(2)
C(41)–C(42)	1.385(4)	C(50)–N(51)–Cu(1)	127.61(17)
C(42)–C(43)	1.362(5)	C(46)–N(51)–Cu(1)	114.32(16)
C(43)–C(44)	1.377(5)	N(41)–C(41)–C(42)	121.9(3)
C(44)–C(45)	1.385(4)	C(43)–C(42)–C(41)	119.2(3)
C(45)–C(46)	1.475(4)	C(42)–C(43)–C(44)	119.7(3)
C(46)–C(47)	1.391(4)	C(43)–C(44)–C(45)	118.5(3)
C(47)–C(48)	1.377(4)	N(41)–C(45)–C(44)	121.9(3)
C(48)–C(49)	1.375(4)	N(41)–C(45)–C(46)	114.6(2)
C(49)–C(50)	1.375(4)	C(44)–C(45)–C(46)	123.6(2)
		N(51)–C(46)–C(47)	122.0(2)
		N(51)–C(46)–C(45)	114.5(2)

TABLE III (*Continued*)

C(47)–C(46)–C(45)	123.5(2)
C(48)–C(47)–C(46)	119.1(3)
C(49)–C(48)–C(47)	118.9(3)
C(48)–C(49)–C(50)	119.3(3)
N(51)–C(50)–C(49)	122.7(2)

Hydrogen bonds

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
O(1)–H(101)···O(22)	0.82(4)	1.98(4)	2.786(3)	166(4)
O(2)–H(201)···O(1)	0.89(4)	1.99(4)	2.873(4)	173(4)
O(1)–H(102)···O(4)#4	0.72(4)	2.06(4)	2.766(5)	171(4)
O(2)–H(202)···O(1)#5	0.90(5)	1.88(5)	2.769(4)	169(4)
O(3)–H(301)···O(2)#6	1.06(2)	1.80(2)	2.798(4)	155.4(19)
O(3)–H(302)···O(12)#4	0.88(4)	1.86(4)	2.717(4)	164(4)
O(31)–H(310)···O(22)#1	0.68(3)	2.10(3)	2.768(4)	175(4)
O(4)–H(401)···O(12)#6	0.65(4)	2.07(4)	2.719(4)	171(5)
O(4)–H(402)···O(2)#1	0.84(4)	2.13(4)	2.927(5)	159(4)

Symmetry transformations used to generate equivalent atoms: (i) = #1 = $-x, y+1, -z+1$, (ii) = #2 = $x-1, y, z$, (iii) = #3 = $x+1, y, z$ (iv) = #4 = $-x+1, -y+1, -z+1$, (v) = #5 = $-x, -y+2, -z$, (vi) = #6 = $x, y, z+1$.

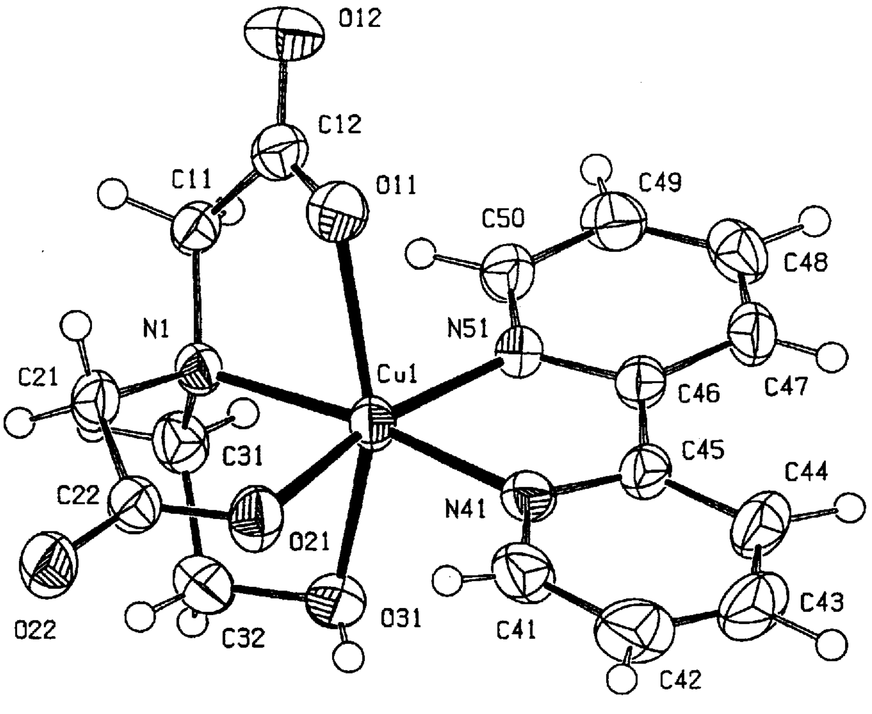


FIGURE 1 The complex molecule in compound I, [Cu(heida)(bipy)]·$4H_2O$, with the atom numbering scheme.

In the studied compound the main source of distortion at the coordination polyhedron arises not only from the largest *trans*-apical bonds (Cu(1)–O(11, apical carboxylato), and Cu(1)–O(31, hydroxyl), 2.337(2) and 2.459(2) Å, respectively) but also from unequal *trans*-angles (N(41)–Cu(1)–N(1) (173.2°), N(51)–Cu(1)–O(21) (168.8°) and O(11)–Cu(1)–O(31) (151.6°)). Bond lengths and angles of the coordination polyhedron and ligands in compound I have relatively normal values in agreement with those reported for related compounds $[Cu(IDA)(H_2O)_2]$[1–3] and $[Cu(heida)(H_2O)]\cdot H_2O$[16] or having a 1/1/2 Cu(II)/IDA/*N*-heterocyclic donor ratio such as $[Cu(IDA)(Him)_2]_2\cdot 2H_2O$,[15] $[Cu(IDA)(bipy)]\cdot 6H_2O$[16] and $[Cu(heida)(phen)]\cdot 7H_2O$.[19] This is true for both Cu(II)–*N*(heterocyclic) bonds, Cu–N(41) (1.994(2) Å) and Cu–N(51) (2.053(3) Å), which have similar lengths in I to the corresponding bonds in $[Cu(IDA)(Him)_2]_2\cdot 2H_2O$ (1.981(1) and 1.987(1) Å), $[Cu(IDA)(bipy)]\cdot 6H_2O$ (1.986(3) and 2.047(3) Å and $[Cu(heida)(phen)]\cdot 7H_2O$ (1.992(3) and 2.058(3) Å). The clear preference of the *N*(heterocyclic) atoms of bipy (and phen) by two among the four closest donors of copper(II) does not preclude heida to act as a tripodal tetradentate ligand. However, this modifies significantly Cu–heida bond lengths and the heida conformation. In this connection, it should be noted that the Cu(1)–N(1) bond (2.075(2) Å) is larger than the same bond in the parent compound $[Cu(heida)(H_2O)]\cdot H_2O$ (2.00(1) Å[16]) and in the closely related complex $[Cu(heida)(phen)]\cdot 7H_2O$ (2.059(4) Å[19]). Obviously in I a carboxylate group is moved to an apical/distal position of copper(II) coordination with subsequent bond lengthening from 1.95(1) Å (average value in $[Cu(heida)(H_2O)]\cdot H_2O$[16] to 2.337(2) Å in I, and 2.332(3) in the related phen derivative). In addition, the Cu–O(hydroxyl) bond is also lengthened from 2.35 Å in $[Cu(heida)(H_2O)]\cdot H_2O$[16] to 2.459(2) Å in I and 2.471(3) Å in the phen analogue.[19]

The internal geometry of bipy and heida are normal. The bipy ligand is planar, with deviations of the atoms from the mean planes of rings containing N(41) and N(51) atoms of $\leq 0.08(2)$ and $\leq 0.06(2)$ Å, respectively. Both planes of pyridine rings define a dihedral angle of 7.7(2)°. The mean plane of the entire bipy ligand (with max. deviations of $\leq 0.09(2)$ Å) define a close dihedral angle (4.4(1)°) with that of the four closest donors of the copper(II) atom. Accordingly, the metal lies only 0.008(1) Å from bipy mean plane. These data are comparable with corresponding values reported for $[Cu(IDA)(bipy)]\cdot 6H_2O$[16] and $[Cu(heida)(phen)]\cdot 7H_2O$.[19] The tripodal tetradentate role of the heida ligand represents the formation of three chelate rings sharing the Cu(1)–N(1) bond. Two are Cu(II)-glycinate-like rings and have unsymmetrical envelope conformations (with both C atoms at the same side of its N–Cu–O plane).[59] We can classify these rings as two different types. One (ring G) is nearly coplanar to the above plane (angle between mean planes of 3.6° and max. deviation of atoms in the ring = 0.15 Å). The other one (ring R) is more distorted (max. deviation of atoms in the ring = 0.24 Å) and it is non-coplanar (indeed nearly perpendicular) to the ring G (angle between mean planes of both rings = 73.3°) and to first plane (angle between this and that of ring R = 72.8°). The remaining chelate ring is a Cu(II)-ethanolamine-like one and it has an asymmetric skew conformation,[59] with different and opposite deviations of the C(31) and C(32) atoms from the plane N(1)–Cu(1)–O(31) (−0.42 and 0.31 Å respectively). This latter plane defines an angle of 89.1 with the mean plane defining the close copper coordination.

It is worth noting the change of heida conformation when passing from $[Cu(heida)(H_2O)]\cdot H_2O$[16] to compound **I** or $[Cu(heida)(phen)]\cdot 7H_2O$.[19] This change can be understood by considering the structural effects that the incoming bidentate heterocycle promotes in the Cu(IDA) chelate moiety. This exhibits a *mer*-conformation (with two G rings) in $[Cu(heida)(H_2O)]\cdot H_2O$[16] but shows *fac*-conformation (with one G ring and another R one) in both bipy and phen derivatives. In spite of this change, heida acts as tripodal tetradentate ligand in the three octahedral complexes. This finding reveals a noticeable conformational flexibility of heida in its coper(II) chelates. A significant conformational flexibility can be inferred in copper(II) complexes of bicine or bheg.[45–49] Both ligands heida and bheg give chelates of the type ML_2 with M(II) = Co and/or Ni and/or Cu[29,31,44,45] acting as tridentate. In addition, it is well established that bicine gives $[Cu(bheg)]ClO_4\cdot H_2O$[49] and compounds of general formula $[Cu(bheg)L']\cdot nH_2O$ (L′ = Cl, Br or NCS) having distorted trigonal bipyramidal Cu(II) coordination,[46–48] as well as $[Cu(bheg)Br(H_2O)]$ (asymmetrical elongated octahedron, type 4 + 1 + 1).[47] In all these compounds bheg acts as tripodal tetradentate ligand and L′ is linked *trans* to the Cu–N(bheg) bond. In the five-coordinate compounds the two O(hydroxyl) donors give Cu–O bonds with different lengths, one 2.00–2.05 Å, and the other 2.18–2.20 Å. The addition of one aqua ligand to transform [Cu(bheg)(Br)] in the six-coordinate derivative $[Cu(bheg)Br(H_2O)]$ does not modify the tetradentate role of bheg (nor the Cu(II)–O(carboxylate) bond) but produces a significant lengthening of the Cu(II)–N(amino) bond (from 2.024(6) to 2.07(1) Å) and both Cu(II)–O(hydroxyl) bonds (from 2.048(6) and 2.194(7) Å to 2.29(1) and 2.67(1) Å).[47] In this octahedral Cu(II)–bheg derivative the two *trans*-Cu(II)–O(hydroxyl) bonds are the longest. In addition, the univalent ligands (bromo and aqua) are necessarily in *cis* positions and they can be compared with the *N,N*-bidentate bipy or phen in compound I and in [Cu(heida)(phen)] · $7H_2O$,[19] respectively. Indeed a comparison of these Cu(II)–heida derivatives reveal lengthening of the Cu(II)–N(amino) bond (from 2.00(1) to 2.075(2) and 2.059(3) Å, respectively), as well as of a Cu(II)–O(carboxylato) bond (from 1.95(1) average to 2.337(2) and 2.322(3) Å, respectively) and the Cu(II)–O(hydroxyl) bond (from 2.35(1) to 2.459(2) and 2.471(3) Å, respectively). Such parallel behaviour in the chelating role of bheg and heida strongly suggests that the basis of its conformational flexibility mainly arises from that of the skewed copper(II)–ethanolamine chelate ring.

The crystal is built up by a hydrogen bond network where the polar O–H bond of the heida ligand hydroxyl group and those ones of water molecules are involved (Table III). Figure 2 shows a plot of the unit cell where complex and water molecules are linked by such hydrogen bonds. The O(1) water is involved in four hydrogen bonds. It acts as donor for an adjacent water molecule and an *O*-carboxylate atom from a neighbouring heida ligand, whereas it displays an acceptor role with two O(2) water molecules of different asymmetric units. The O(2) water molecule is also involved in four hydrogen bonds which relates it with four neighbouring water molecules. In addition, both O(3) and O(4) water molecules act as H-donors in a similar way, for an adjacent one and for an *O*-carboxylate acceptor of a

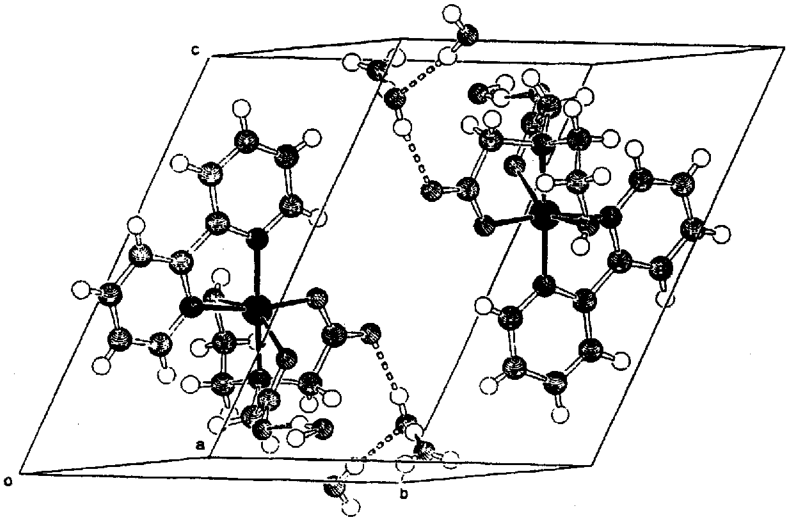


FIGURE 2 Unit cell of compound I.

neighbouring heida ligand. In the broad system of hydrogen bonds building up the crystal of compound I it is worth noting the role of the link O(31)–H(310)$\cdots$O(2^i) (symmetry code $i = -x, -y+1, -z+1$) between the hydroxyl group of an heida ligand and an *O*-carboxylate acceptor of an adjacent one. This unsymmetrical and non-linear link is however that which exhibits the largest angle (175(4)°, see Table III). Moreover two of such hydrogen bonding interactions link two complex molecules which are symmetry related to each other by the inversion centre (Figure 3(a)). The resulting pairs of complex molecules and the lattice water molecules build up a monodimensional supra-molecular network extending along the *a* axis of the crystal (see Figure 3(a) and (b)).

TG/DTG analysis of compound I (6.602 mg, 10°C/min., air flow) reveals its thermal decomposition in three overlapped steps. The first (85–210°C, loss weight ~16.4%, calcd. for $4H_2O$ 15.43%) is mainly (but not only) due to dehydration. The remaining two (210–250°C and 250–~675°C) correspond to pyrolysis of the organic ligands. The residue at 675°C is close to expected for CuO (found 18.75%, calcd. 17.03%). IR spectra of the evolved gases indicate that the first step corresponds not only to the loss of water

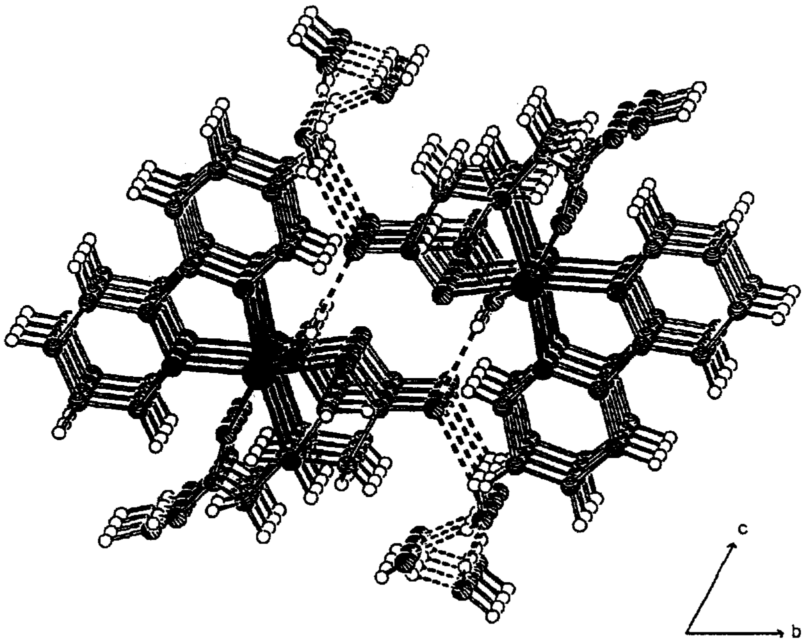


FIGURE 3(a)

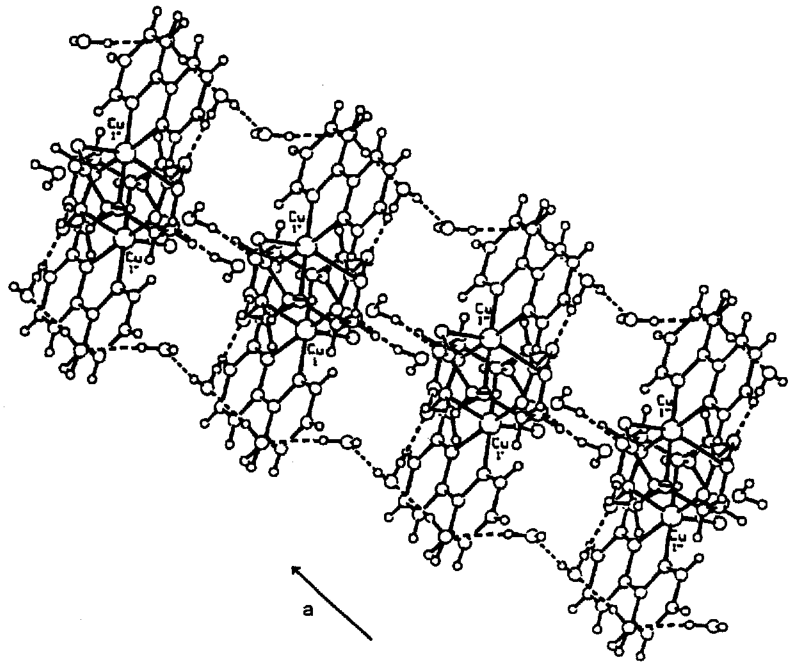


FIGURE 3(b)

FIGURE 3 Supra-molecular network in the crystal of compound I. (a) A projection showing a series of pairs of complex molecules (symmetry related by the inversion centre) linked by the hydrogen bond O(31)–H(310)···O(22^i) (symmetry code $i = -x, -y+1, -z+1$) and the symmetry related one. Some hydrogen bonds involving water molecules are also plotted. (b) Mono-dimensional series of pairs of complex moleules extending along the *a* axis (lying perpendicular to the plane of plot) are hydrogen bonded involving water molecules.

but also to production of CO_2. The amount of these gases in the second step precludes the detection of N_2O, NO or NO_2.

The IR spectrum of the compound is relatively unclear because the overlap of bipy bands with others of water and/or heida. Tentative assignments[60] (wave number in cm^{-1}) are: ν(OH) of water and heida hydroxyl group (~3600–3000, broad), ν(CH atom) (3020), $\nu_{as}(CH_2)$ (2960, 2945), $\nu_s(CH_2)$ (2885), $\delta(H_2O)$ (1620), ν_{as}(COO) (1590 and 1580, s), skeletal bipy ring (1550, shoulder) and ν_s(COO) (1400, s and 1390, shoulder). The two types of carboxylate groups (linked to equatorial or apical coordination sites) are distinguished. The difference $\Delta(COO) = \nu_{as}(COO) - \nu_s(COO) \sim 190\,cm^{-1}$ is in accordance with the predominantly ionic nature of the Cu(II)–O(carboxylato) bonds. The electronic spectrum shows an unsymmetrical d-d band with $\nu_{max} = 14{,}470\,cm^{-1}$ and a shoulder near $12{,}500\,cm^{-1}$

in agreement with the elongated octahedral chromophore CuN_3O_3 (or CuN_3O+O+O). These data can be compared with those reported for the closely related compound $[Cu(IDA(bipy)]\cdot 6H_2O$ ($\nu_{max} = 15{,}100$ and shoulder at $12{,}300\,cm^{-1}$[16a] with an even more unsymmetrical elongated octahedral coordination.[16]

The powder ESR spectrum at room temperature is of axial type but quasi-isotropic with $g_{\|} = 2.17 > g_{\perp} = 2.06 > 2.03$. These data are in accordance[1,2] with a d_{x2-y2} Cu(II) ground state in a mononuclear complex having a CuN_3O+O+O chromophore. The shortest Cu(1)–Cu(1^i) distance is 6.527(2) Å (see Figure 3). A plot of χ data versus T(K) ($T = 80-298$ K) is linear (with statistical r^2 factor of 0.9993) according to Curie–Weiss behaviour. The Curie constant is $C = 0.405\,K\cdot emu\cdot mol^{-1}$ and the Weiss constant is $\theta = 6.45$. The estimated value of μ_{eff} for Cu(II) atom is 1.80 BM, in accordance with the molecular and crystal structure here reported.

A comparison of the structures of $[Cu(heida)(H_2O)]\cdot H_2O$ and $[Cu(heida)(bipy)]\cdot 4H_2O$ (this work) and $[Cu(heida)(phen)]\cdot 7H_2O$ reveals that the *N*,*N*-bidentate in the former compound (occupying two of the four closest sites around the metal) binds without modification of the copper(II) coordination number, type of coordination polyhedron (4 + 1 + 1) and denticity of heida, but with a significant conformational change of the tripodal tetradentate ligand. In the parent compound $[Cu(heida)(H_2O)]\cdot H_2O$ the Cu-(IDA) chelate moiety exhibits *mer*-configuration, whereas in the last two derivatives it binds in *fac* mode. Such a conformational change represents lengthening of three bonds [Cu–N(amino), one of two Cu–O(carboxylato) and Cu–O(hydroxyl)]. On the basis of these results and those concerning copper(II)-bicine derivatives, the conformational flexibility of heida (and bicine) is attributed to that of the skewed Cu(II)–ethanolamine ring.

Acknowledgements

AC thanks the Xunta de Galicia for financial support (Project XUGA20309B97). A research grant to EBA from Ministerio de Educación y Cultura is gratefully acknowledged. We are grateful to the Dirección General de Enseñanza Superior e Investigación Científica, MEC, Spain, for financial support (Project PB-98-0605-C03-03).

References

[1] F.G. Kramanenco, T.N. Polynova, M.A. Porai-Koshits, V.P. Chalvi, G.N. Kumivanova and L.I. Martynenko, *Zh. Strukt. Khim.*, 14, 744 (1973).

[2] A. Podder, J.K. Dattagupta, N.N. Saha and N. Saenger, *Acta Crystallogr.*, **B35**, 53 (1979).

[3] M.J. Román-Alpiste, J.D. Martin-Ramos, A. Castiñeiras-Campos, E. Bugella-Altamirano, A.G. Sicilia-Zafra, J.M. González-Pérez and J. Niclós-Gutiérrez, *Polyhedron*, **18**, 3341 (1999).

[4] X. Duanjun, C. Chaorong, X. Yuanzhi and Z. Kangjing, *Jiegou Xuaxue*, **6**, 39 (1987).

[5] X. Duanjun, C. Chaorong, X. Yuanzhi and Z. Kangjing, *Jiegou Xuaxue*, **6**, 106 (1987).

[6] J.M. González Pérez, N.-H. Dung, J. Niclós-Gutiérrez, B. Viossat, A. Busnot and M.L. Vicente-Gelabert, *Inorg. Chim. Acta*, **166**, 115 (1989).

[7] N.-H. Dung, B. Viossat, A. Busnot, J.M. Pérez, J. Niclós Gutiérrez and F. Gardette, *Inorg. Chim. Acta*, **174**, 145 (1990).

[8] J. Niclós Gutiérrez, E. Abarca Garcia, B. Viossat, N.-H. Dung, A. Busnot and J.F. Hemidy, *Acta Crystallogr.*, **C49**, 19 (1993).

[9] A. Castiñeiras Campos, A. Busnot, M.E. Abarca-Garcia, A.G. Sicilia-Zafra, J.M. González Pérez and J. Niclós Gutiérrez, *Inorg. Chim. Acta*, **215**, 73 (1994).

[10] A. Castiñeiras Campos, J.M. Tercero, A. Matilla, J.M. González, A.G. Sicilia and J. Niclós, *J. Coord. Chem.*, **35**, 61 (1995).

[11] A. Castiñeiras-Campos, A.G. Sicilia Zafra, J.M. González-Pérez, J. Niclós Gutiérrez, E. Chinea and A. Mederos, *Inorg. Chim. Acta*, **241**, 39 (1996).

[12] A.G. Sicilia-Zafra, E. Bugella-Altamirano, J.M. González-Pérez, J.D. Martín-Ramos and J. Niclós-Gutiérrez, *VIII Italian–Spanish Congress on Thermodynamics of Metal Complexes*, Cagliari, Italy, 1997, p. 56.

[13] E. Bugella Altamirano, J.M. González Pérez, A.G. Sicilia Zafra, J.D. Martín Ramos, A. Castiñeiras-Campos and J. Niclós Gutiérrez, 'Low molecular compounds as bioinorganic models: Mixed-ligand copper(II) complexes with N-protected N-carboxymethylglycinato(2-) and N-protected-imidazole ligands', *I Virtual Congress about Pharmacy*, University of Granada, Granada, Spain, (1998); http://www.ugr.es/~genfarma/bien.htm.

[14] (a) M.J. Román, J.D. Martín, A.G. Sicilia, E. Bugella, J.M. González and J. Niclós, *IX Spanish–Italian Congress on Thermodynamics of Metal Complexes*, Girona, Spain, 1998, Report C-10; (b) E. Bugella, A.G. Sicilia, J.M. González, A. Castiñeiras and J. Niclós, *IX Spanish–Italian Congress on Thermodynamics of Metal Complexes*, Girona, Spain, 1998, Report P-2; (c) A. Castiñeiras, A.G. Sicilia, J.M. González, E. Bugella and J. Niclós, *IX Spanish–Italian Congress on Thermodynamics of Metal Complexes*, Girona, Spain, 1998, Report P-5; (d) M.J. Román, J.D. Martín, A.G. Sicilia, E. Bugella, J.M. González and J. Niclós, *IX Spanish–Italian Congress on Thermodynamics of Metal Complexes*, Girona, Spain, 1998, Report P-31.

[15] N.-H. Dung, B. Viossat, A. Busnot, A.G. Sicilia Zafra, J.M. González Pérez and J. Niclós Gutiérrez, *Inorg. Chim. Acta*, **169**, 9 (1990).

[16] (a) G. Nardin, L. Randaccio, R.P. Bonomo and E. Rizzareli, *J. Chem. Soc., Dalton Trans.*, 369 (1980); (b) A. Castiñeiras, M.E. Abarca, I.S. de la Cueva, J.M. González and J. Niclós, *J. Coord. Chem.*, **30**, 273 (1993).

[17] I.S. de la Cueva, A.G. Sicilia, J.M. González, E. Bugella, A. Castiñeiras and J. Niclós-Gutiérrez, *React. Funct. Polym.*, **36**, 211 (1998).

[18] J.M. González, A.G. Sicilia, I.S. de la Cueva, M.E. Abarca, A. Castiñeiras Campos and J. Niclós Gutiérrez, *VII Spanish–Italian and Mediterranean Congress on Thermodynamics of Metal Complexes*, Granada, Spain, 1996, Report 2-P-07.

[19] O.P. Gladkikh, A.L. Poznyak, T.N. Polynova and M.A. Porai-Koshits, *Russ. J. Coord. Chem.*, **23**, 166 (1997).

[20] A. Castiñeiras Campos, J.D. Martín Ramos, E. Bugella Altamirano, J.M. González Pérez, D. Choquesillo Lazarte and J. Niclós Gutiérrez, *X Italian–Spanish Congress on Thermodynamics of Metal Complexes*, S. Martino al Cimino, Italy, 1999, Report C-18.

[21] A. Castiñeiras Campos, E. Bugella Altamirano, J.M. González Pérez, D. Choquesillo Lazarte and J. Niclós Gutiérrez, unpublished results.

[22] E. Bugella-Altamirano, J.M. González-Pérez, A.G. Sicilia Zafra, J. Niclós-Gutiérrez and A. Castiñeiras-Campos, *Z. Anorg. Allg. Chem.*, **626**, 1 (2000).

[23] N. Bresciani-Pahor, G. Nardin, R.P. Bonomo and E. Rizzarelli, *J. Chem. Soc., Dalton Trans.*, 2625 (1984).

[24] G.J. Colpas, B.J. Hamstra, J.W. Kampf and V.L. Pecoraro, *J. Am. Chem. Soc.*, **116**, 3627 (1994).

[25] G.J. Colpas, B.J. Hamstra, J.W. Kampf and V.L. Pecoraro, *J. Am. Chem. Soc.*, **118**, 3469 (1996).

[26] M. Mahroof-Tahir, A.D. Keramidas, R.B. Goldfarb, O.P. Anderson, M.M. Miller and D.C. Crans, *Inorg. Chem.*, **36**, 1657 (1997).

[27] B.J. Hamstra, A.L.P. Houseman, G.J. Colpas, J.W. Kampf, R. Lo Brutto, W.D. Frasch and V.L. Pecoraro, *Inorg. Chem.*, **36**, 4866 (1997).

[28] N.N. Anan'eva, T.N. Polynova and M.A. Porai-Koshits, *Koord. Khim.*, **7**, 1556 (1981).

[29] I.N. Polyakova, T.N. Polynova and M.A. Porai-Koshits, *Koord. Khim.*, **8**, 1268 (1982).

[30] O.P. Gladkikh, T.N. Polynova and M.A. Porai-Koshits and A.L. Poznyak, *Koord. Khim.*, **19**, 43 (1993).

[31] (a) I.N. Polyakova, T.N. Polynova and M.A. Porai-Koshits and N.D. Mitrofanova, *Zh. Strukt. Khim.*, **19**, 765 (1978); (b) I.N. Polyakova, T.N. Polynova and M.A. Porai-Koshits, *Koord. Khim.*, **8**, 1268 (1982).

[32] I.N. Polyakova, T.N. Polynova and M.A. Porai-Koshits, *Koord. Khim.*, **7**, 1894 (1981).

[33] (a) N.N. Aman'eva, I.N. Polynova, T.N. Polynova, M.A. Porai-Koshits and N.D. Mitrofanova, *Zh. Strukt. Khim.*, **16**, 481 (1975); (b) N.N. Anan'eva, I.N. Polynova, J.N. Polynova and M.A. Porai-Koshits, *Koord. Khim.*, **7**, 1578 (1981).

[34] A.S. Antsyshkina, L.M. Shkol'nikova, G.G. Sadikov, V.S. Sergienko and R.L. Davidovich, *Zh. Neorg. Khim.*, **40**, 1263 (1995).

[35] (a) I.N. Polyakova, T.N. Polynova, M.A. Porai-Koshits and A.M. Grevtsev, *Zh. Strukt. Khim.*, **20**, 555 (1979); (b) I.N. Polyakova, T.N. Polynova and M.A. Porai-Koshits, *Koord. Khim.*, **7**, 1737 (1981).

[36] (a) I.N. Polyakova, T.A. Senina, T.N. Polynova, M.A. Porai-Koshits and N.D. Mitrofanova, *Zh. Strukt. Khim.*, **18**, 1128 (1977); (b) I.N. Polyakova, T.A. Senina, T.N. Polynova and M.A. Porai-Koshits, *Koord. Khim.*, **9**, 1131 (1983).

[37] (a) I.N. Polyakova, T.N. Polynova, M.A. Porai-Koshits and N.D. Mitrofanova, *Zh. Strukt. Khim.*, **19**, 766 (1978); (b) I.N. Polyakova, T.N. Polynova and M.A. Porai-Koshits, *Koord. Khim.*, **9**, 1563 (1983).

[38] A.B. Ilykhin and R.L. Davidovich, *Koord. Khim.*, **20**, 590 (1994).

[39] Y.-T. Khuan, C.-D. Khu, L.M. Shkol'nikova and R.L. Davidovich, *Koord. Khim.*, **21**, 891 (1995).

[40] A. Meriem, R. Willem, J. Meunier-Piret and M. Gielen, *Main Group Metal Chem.*, **12**, 187 (1989).

[41] L.M. Shkol'nikova and A.E. Obodovskaya, *Zh. Strukt. Khim.*, **27**, 125 (1986).

[42] Z. Sun, P.K. Gantzel and D.N. Hendrickson, *Polyhedron*, **16**, 3267 (1997).

[43] Z. Sun, P.K. Gantzel and D.N. Hendrickson, *Polyhedron*, **17**, 1511 (1998).

[44] E.B. Chuklanova, T.N. Polynova, M.A. Porai-Koshits and G.K. Babeshkina, *Koord. Khim.*, **7**, 944 (1981).

[45] (a) N.N. Anan'eva, N.I. Samus, T.N. Polynova, M.A. Porai-Koshits and N.D. Mitrofanova, *Zh. Strukt. Khim.*, **16**, 480 (1975); (b) N.N. Anan'eva, N.I. Sorokina, T.N. Polynova and M.A. Porai-Koshits, *Vestn. Mosk. Univ., Ser. Khim.*, **22**, 58 (1981).

[46] H. Yamauchi, Y. Inomato and T. Takeuchi, *Inorg. Chim. Acta*, **172**, 105 (1990).

[47] H. Yamauchi, Y. Inomato and T. Takeuchi, *Inorg. Chim. Acta*, **181**, 31 (1991).

[48] H. Yamauchi, M. Nagase, Y. Yukawa, Y. Inomato and T. Takeuchi, *Bull. Chem. Soc. Jpn.*, **61**, 2763 (1988).

[49] H. Yamauchi, Y. Inomata and T. Takeuchi, *Inorg. Chim. Acta*, **161**, 217 (1989).

[50] W.B. Gwenther, *Quantitative Chemistry: Measurements and Equilibrium* (Addison-Wesley Publishers, Massachusetts, 1968).

[51] *ENRAF-NONIUS CAD-4 Software, Versión 5.0*, (Enraf-Nonius, Delft, The Netherlands, 1989).

[52] A.L. Spek, *HELENA; A Program for Data Reduction of CAD4 Data* (University of Utrecht, The Netherlands, 1997).

[53] G.M. Sheldrick, *Acta Crystallogr.*, **A46**, 467 (1990).

[54] G.M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structures* (University of Göttingen, Germany, 1997).

[55] *International Tables X-ray Crystallography*, Vol. C (Kluwer Academic Publishers, Dordrecht, The Nederlands, 1995).
[56] L. Zsolnai and M. Krestchmar, *ZORTEP. A Program for the Presentation of Thermal Ellipsoids* (University of Heidelbergend Tübingen, Germany, 1997).
[57] E. Keller, *SCHAKAL. Program for Plotting Molecular and Crystal Structures* (University of Freiburg, Germany, 1998).
[58] F.E. Mabbs and D.J. Machin, *Magnetism and Transition Metal Complexes* (Chapman and Hall, London, 1973).
[59] C.J. Hawkins, *Absolute Configuration of Metal Complexes* (Wiley-Interscience, New York, 1971), Chap. 3.
[60] L.J. Bellamy, *The Infrared Spectra of Complex Molecules*, 3rd edn. Vol. 1, (Chapman and Hall, London, 1975).