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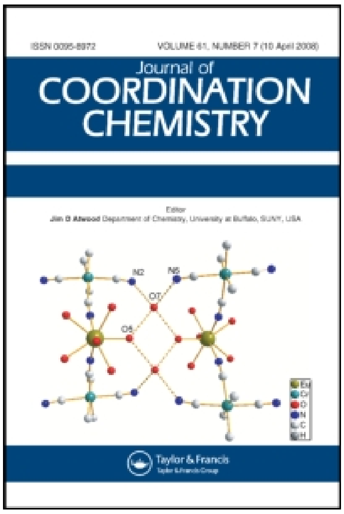

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Synthesis and Characterization of Tris(2,2'-bipyridine) and tris(1,10-phenanthroline) Copper(II) Hexafluorophosphate. Crystal Structure of the Phenanthroline Complex

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SYNTHESIS AND CHARACTERIZATION OF TRIS(2,2′-BIPYRIDINE) AND TRIS(1,10-PHENANTHROLINE) COPPER(II) HEXAFLUOROPHOSPHATE. CRYSTAL STRUCTURE OF THE PHENANTHROLINE COMPLEX

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The tris-(bidentate)chelate complexes $[Cu(NN)_3](PF_6)_2$ where NN = 2,2′-bipyridine or 1,10-phenanthroline have been isolated as secondary products in the reaction between the dimers $[\{Cu(NN)\}_2(\mu\text{—}OH)_2](PF_6)_2 \cdot 2H_2O$ and di-2-pyridylketone. The X-ray crystal structure of $[Cu(phen)_3](PF_6)_2$ showed a distorted octahedral C_2 geometry around the metal atom, with two Cu—N distances being much longer than the other four. Magnetic susceptibility measurements (in the 4.4–290 K range) correspond, in both cases, to a d^9 configuration without significant magnetic interaction. A signal (g = 2.102) was observed in the EPR spectrum of the bipy complex and the two axial components were resolved for the phen complex, with $g_{\|} = 2.249$, $g_{\perp} = 2.083$ and $A_{\|} = 137 \times 10^{-4}\,cm^{-1}$. In this case also a signal at g = 2.128 is observed.

Keywords: Tris(bibentate) chelates; 2,2′-bipyridine; 1,10-phenanthroline; Crystal structure

INTRODUTION

The monomers, tris(bidentate) chelate complexes $[Cu(NN)_3]X_2$ where NN = 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) and $X^- = PF_6^-$

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or ClO_4^-, have been isolated as secondary products in the reaction between the dimers $[\{Cu(NN)\}_2(\mu—OH)_2]X_2 \cdot 2H_2O$ and di-2-pyridylketone [1]. The perchlorate complexes have been already described [2, 3]. A crystal structure determination of $[Cu(phen)_3](ClO_4)_2$ [3] allowed to examine for the first time the existence of a "normal" Jahn Teller distortion in tris(bidentate) chelate complexes of Cu(II) with four short Cu—N bonds and two equal long Cu—N bonds. The coordination geometry of Cu(II) in tris(bidentate) chelate complexes may range from a tetragonal distortion to cases without apparent Jahn Teller distortion as in $[Cu(en)_3](SO_4)_2$ [4], through less symmetric distortions. Compounds with $X^- = NO_3^-$ and $TCNQ^-$ (tetracyanoquinodimethanide) have been also described [5, 6].

Many systems such as $[Cu(NN)_2X]Y$ with a great variety of structural characteristics have been studied [7–10]. $[Cu(bipy)_2](PF_6)_2$ [11] has been described. In this paper we report the preparation and characterization of $[Cu(bipy)_3](PF_6)_2$ and $[Cu(phen)_3](PF_6)_2$ and the crystal structure of the latter.

EXPERIMENTAL

Synthesis of $[Cu(bipy)_3](PF_6)_2$ (1) and $[Cu(phen)_3](PF_6)_2$ (2)

In the synthesis of Cu(II) dimers with methoxydi(2-pyridyl)methoxide as bridging ligand by the reaction between $[\{Cu(NN)\}_2(\mu\text{-}OH)_2](PF_6)_2 \cdot 2H_2O$ (NN = 2,2′-bipyridine or 1,10-phenanthroline) and di-2-pyridylketone [1], blue crystals of the monomers $[Cu(NN)_3](PF_6)_2$ were obtained when the volume of the reaction solution was reduced.

Compound **1**, dec. 238°C. *Anal.* calcd. for $C_{30}CuF_{12}H_{24}N_6P_2$ (%): Cu, 7.73; C, 43.83; H, 2.94; N, 10.22. Found: Cu, 7.65; C, 43.48; H, 2.91; N, 10.11.

Compound **2**, dec. 246°C. *Anal.* calcd. for $C_{36}CuF_{12}H_{24}N_6P_2$ (%): Cu, 7.11; C, 48.36; H, 2.71; N, 9.40%. Found: Cu, 7.21; C, 48.23; H, 2.68; N, 9.38.

Measurements

C, H and N were analysed using a Perkin-Elmer 240 C instrument. Copper was determined with a Perkin-Elmer 2380 AAS ($\lambda = 324.8$ nm). Melting (dec.) points were measured on an Electrothermal 9300 instrument. Conductivity measurements were made using a Metrhom E518 conductimeter.

IR spectra were recorded on a Nicolet FT-IR 510 spectrometer in the range $4000-400\,cm^{-1}$ using KBr pellets and on a Nicolet 740 in $650-50\,cm^{-1}$ using nujol on a polyethylene film. Electronic spectra were recorded on a Schimadzu UV-265 FW spectrophotometer.

Magnetic measurements were carried out in the $290-4.4$ K range with a magnetometer (Manics DSM8) equipped with an He continuous flow cryostat and a Drusch EAF 16UE electromagnet. EPR spectra were recorded on a Bruker ESP 300 spectrometer with a Bruker ER 035 M gaussmeter, Oxford ITC4 cryostat and HP 5325B frequency counter.

Crystal Structure Determination of [Cu(phen)$_3$](PF$_6$)$_2$

X-ray diffraction data were collected at 293 K with a Siemens P4 diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å), operating in the ω scanning mode. The unit cell parameters were determined from 25 random reflections. Three standard reflections were measured every 60 minutes, showing no significant decay. Data were corrected for Lorentz and polarization effects but not for absorption.

Crystallographic data, conditions used for the data collection and features of the structure refinement are listed in Table I.

TABLE I Crystallographic and refinement data for $[Cu(phen)_3](PF_6)_2$

Empirical formula	$C_{36}CuF_{12}H_{24}N_6P_2$
Formula weight	894.09
Crystal dimensions (mm)	0.35 × 0.3 × 0.23
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions:	
a(Å)	54.836(8)
b(Å)	15.9230(1)
c(Å)	12.2990(1)
β(°)	94.382(9)
Volume (Å^3)	10708(2)
Z	12
Calculated density ($g\,cm^{-3}$)	1.664
Absorption coefficient (mm^{-1})	0.803
F(000)	5388
θ range for data collection (°)	1.70 to 22.50
Limiting indices	$(-1, -1, -13)$ to $(58, 17, 13)$
Collected reflections	8835
Independent reflections	7006 ($R_{int} = 0.0330$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6978/0/771
Goodness-of-fit on F^2	1.105
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0883$, $wR2 = 0.2557$
R indices (all data)	$R1 = 0.1446$, $wR2 = 0.4038$
Largest diff. peak and hole (eÅ^{-3})	1.462 and -1.352

The structure was solved by direct methods and refined by full-matrix least-squares on F^2, using the weighting scheme $w^{-1} = \sigma^2(F_o)^2 + (0.20\,P)^2 + 150\,P$, where $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in their ideal positions. The program package SHELXTL-V5 [12] was used for structure solution and refinement and for the drawings. Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-138345. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk). Structure factor data are available from the authors upon request.

RESULTS AND DISCUSSION

Characterization

The molar conductivity values for **1** and **2** in acetonitrile solutions, $295\,\Omega^{-1}\,\text{cm}^2\,\text{mol}^{-1}$ in both cases, and the slope of the plot of the equivalent conductivity *versus* the square root of the equivalent concentration, 630 (**1**) and 624 (**2**), indicate that the complexes behave as 1:2 electrolytes [13, 14]. IR spectra of **1** and **2** show bands described for various compounds with $[\text{Cu(NN)}_3]^{2+}$ cations [15–17]. Characteristic bands of the PF_6^- group occur at $836\,\text{cm}^{-1}$ [$\text{v}_3(\text{F}_{1u})$] and $557\,\text{cm}^{-1}$ [$\text{v}_4(\text{F}_{1u})$] for **1** and $837\,\text{cm}^{-1}$ [$\text{v}_3(\text{F}_{1u})$] and $557\,\text{cm}^{-1}$ [$\text{v}_4(\text{F}_{1u})$] for **2**. Electronic spectra of acetonitrile solutions of **1** and **2** exhibit, besides the ligand bands, the d-d band of Cu(II) at 675 nm in acetonitrile solution and at 680 nm in diffuse reflectance spectra.

Crystal Structure of $[\text{Cu(phen)}_3](\text{PF}_6)_2$

The compound is a simple ionic crystal built up by $[\text{Cu(phen)}_3]^{2+}$ cations and PF_6^- anions. Two crystallographically independent cations are present; one of them occupies a general position, Cu(1), and the other, Cu(2), lies on a crystallographic twofold axis that bisects one of the phenanthroline molecules (that labelled with F; Figs. 1 and 2). The most significant interatomic distances and angles are listed in Table II.

The geometry around each metal atom is octahedral with the expected deviations in bond angles due to the bite of the ligand. As expected, the ideal D_3 symmetry is decreased to C_2 due to the Jahn-Teller effect, two of the

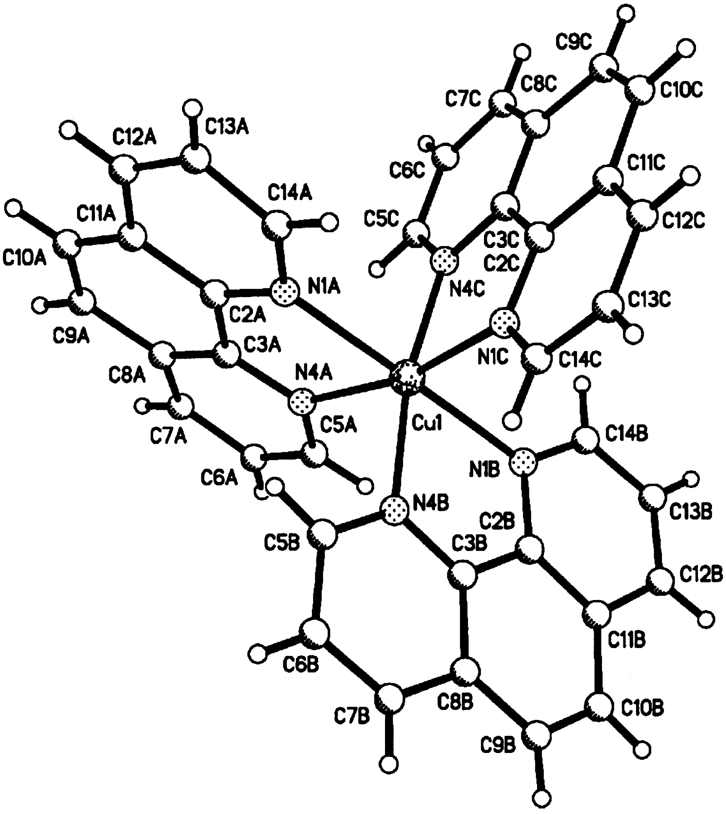

FIGURE 1 Structure of the $[Cu(phen)_3]^{2+}$ cation in position 1.

Cu—N distances being much longer than the other four. The geometrical parameters are comparable to those previously published for the $[Cu(phen)_3]^{2+}$ cation. Around Cu(1) the short and long Cu—N mean distances (2.052 and 2.293 Å, respectively) are similar to those found for $[Cu(phen)_3](ClO_4)_2$ (2.037 and 2.328 Å) [3]. In the Cu(2) position the difference between short and long distances is smaller. The mean short distance is 2.084 Å and the long one 2.169 Å. This fact is also observed in $[Cu(phen)_3](TCNQ)_2$, where these values are 2.09 and 2.23 Å, respectively [6].

Magnetic and EPR Results

Variable temperature magnetic susceptibility data for **1** and **2** have been recorded between 4.4 and 290 K. The molar magnetic susceptibility per

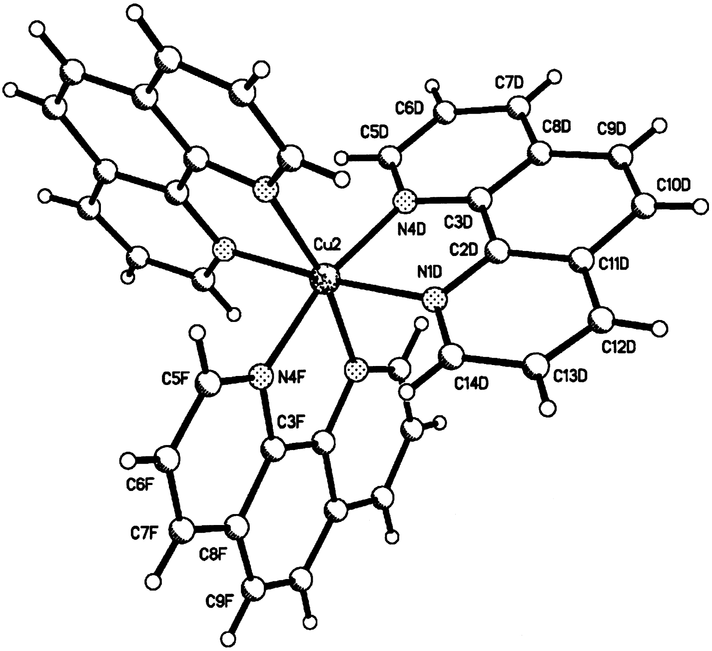

FIGURE 2 Structure of the $[Cu(phen)_3]^{2+}$ cation in position 2.

TABLE II Selected interatomic distances (Å) and angles (°) for $[Cu(phen)_3](PF_6)_2$

Interatomic distances (Å):			
Cu(1)—N(1A)	2.283(10)	Cu(2)—N(4D)	2.083(11)
Cu(1)—N(1B)	2.303(9)	Cu(2)—N(4F)	2.085(10)
Cu(1)—N(1C)	2.063(10)	Cu(2)—N(1D)	2.169(10)
Cu(1)—N(4A)	2.048(10)	Cu(2)—N(4D′)	2.083(11)
Cu(1)—N(4B)	2.043(9)	Cu(2)—N(4F′)	2.085(10)
Cu(1)—N(4C)	2.055(9)	Cu(2)—N(1D′)	2.169(10)
Bond angles (°):			
N(1A)—Cu(1)—N(4A)	76.2(4)	N(1D)—Cu(2)—N(4D)	78.0(4)
N(1B)—Cu(1)—N(4B)	75.9(4)	N(4F)—Cu(2)—N(4F′)	79.4(5)
N(1C)—Cu(1)—N(4C)	81.1(4)	N(1D′)—Cu(2)—N(4D′)	78.0(4)

* Primed atoms related by $-x, y, (1/2)-z$.

Cu(II), corrected from $TIP = 60 \times 10^{-6}\,cm^3\,mol^{-1}$, obeys the Curie-Weiss law. The magnetic moments, 1.82 MB for **1** and 1.85 MB for **2**, correspond to the d^9 configuration of Cu(II) without significant magnetic interaction.

The EPR Q-band spectra at room temperature show a slightly asymmetric signal for **1**, at $g = 2.102$. For compound **2** the two axial components are resolved, $g_{\|} = 2.249$ and $g_{\perp} = 2.083$, and the four hyperfine signals in $g_{\|}$, with $A_{\|} = 137 \times 10^{-4}\,\mathrm{cm}^{-1}$, are observed. These signals are assigned to the Cu(II) in Cu(1) positions. Furthermore a signal at $g = 2{,}128$, assigned to Cu(II) in the less distorted Cu(2) position, is observed.

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