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Short Communication

Crystal Structure and Spectroscopic Properties of the Bis[(*S*-thiocyanate)(2,2′-dipyridylamine)] Copper(II) Complex

José L. Mesa,*[,a] Karmele Urtiaga,[b] Luis Lezama[a] and María I. Arriortua[b]

[a]Department of Inorganic Chemistry and [b]Department of Mineralogy–Petrology, Faculty of Science, University of the Basque Country, Apdo. 644, E-48080 Bilbao, Spain

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The 2,2′-dipyridylamine (dpa, $C_{10}N_3H_9$) ligand has several possible configurations for coordination: the *anti–anti* configuration, refering to the relation of the pyridyl nitrogens to the amine hydrogen, has been found in many bidentate chelate complexes;[1–5] the *syn–syn* configuration occurs in trinuclear complexes,[6–8] and the *anti–syn* configuration exists in the dimer of free ligand.[9] The ability of dpa to coordinate as a bidentate ligand to transition-metal cations, particularly to copper(II), has been extensively investigated.[9–13] The two ring nitrogen atoms act as the electron-pair donors in the majority of compounds, although in some instances the bridging amine nitrogen appears to have donor properties.[14] In recent years several bis(2,2′-dipyridylamine)copper(II) complexes have been prepared and studied.[3,4,15,16] Likewise, the amine proton of the 2,2′-dipyridylamine ligand can be removed, giving rise to monomeric complexes with the [Cu(dpa)$_2$] formula[2] or to more complex polynuclear species[6] in which the 2,2′-dipyridylamine molecule acts as an anionic ligand.

Recently, we have begun a study of polynuclear complexes of bivalent transition metals (Ni^{2+}, Mn^{2+}, Cu^{2+},...) with bidentate ligands such as 2,2′-bipyridine and di-(2-pyridyl)ketone, together with the azido (N_3^-) group. In this way, several polynuclear complexes with a 1:1 or 1:2 ratio of metal to ligand, exhibiting interesting magnetic properties, have been obtained.[17–20] On the other hand, $[M(L_{II})_2X_2]$ complexes, where M is a bivalent transition metal, L_{II} is a bidentate ligand and X is a pseudohalide ligand, can be used as precursors of condensed systems such as $[M(L_{II})_2X](Y)$, in which Y is a noncoordinating anion. Indeed, when an X ligand is extruded from the monomer complex the capability of the remaining pseudohalide group (X) to bridge metallic centres favours stacking of the resulting $[M(L_{II})_2X]^+$ entities. As a consequence, polynuclear complexes of nickel(II) of the type $[Ni(bipy)_2(N_3)](Y)$ ($Y = ClO_4^-$ and PF_6^-) have already been studied.[17] In order to determine the influence of the NCS^- pseudohalide ligand in the structure of this kind of complex we have synthesized and studied the title compound.

Experimental

Synthesis of the compound. The $[Cu(dpa)_2(SCN)_2]$ complex was synthesized by the addition of $CuCl_2 \cdot 2H_2O$ (0.099 g, 0.584 mmol) dissolved in water to an ethanolic solution of 2,2′-dipyridylamine (0.200 g, 1.168 mmol). The resulting solution was treated with a slight excess of KNCS (0.150 g, 1.543 mmol) giving rise to a green precipitate. It was separated by filtration, washed with water and diethyl ether and dried over P_2O_5 for 1 h. Green prismatic crystals suitable for X-ray analysis were obtained by recrystallization from a methanol:water (1:1) solution. Found: C, 50.1; H, 3.0; N, 21.1; Cu, 12.0. Calc. for $C_{22}H_{18}N_8S_2Cu$: C, 50.6; H, 3.4; N, 21.5; Cu, 12.2%. The density was measured by the flotation method in a mixture of CH_2Cl_2/CCl_4.

Physical measurements. The IR spectrum (KBr pellet) was obtained using a Nicolet FT-IR 740 spectrophotometer in the 4000–400 cm^{-1} region. The diffuse reflectance spectrum was registered at room temperature on a Cary 2415 spectrometer in the 5000–45 000 cm^{-1} range. A Bruker ESP 300 spectrometer, operating in the X and Q bands, was used to record the EPR poly-

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* To whom correspondence should be addressed.

crystalline spectra between 4.2 and 300 K. The temperature was stabilized by an Oxford Instruments (ITC 4) regulator. The magnetic field was measured with a Bruker BNM 200 gaussmeter, and the frequency inside the cavity was determined using a Hewlett-Packard 5352B microwave frequency counter.

Crystal structure determination. Diffraction data were collected at room temperature on an Enraf-Nonius CAD4 automated diffractometer using graphite-monochromated Mo $K\alpha$ radiation. Details of crystal data, intensity collection and some features of the structure refinement are reported in Table 1. Lattice constants were obtained by a least-squares refinement of the setting angles of 25 reflections in the range $6 < \theta < 13°$. Intensities and angular positions of two standard reflections were measured each hour: these showed neither decrease nor misalignment during data collection.

Direct methods (SHELXS 86)[21] were employed to solve the structure. The metal atom, which occupies a special position, was first found. The localization of the remaining atoms was achieved by successive application of difference Fourier maps. The structure was then refined by the full-matrix least-squares method based on F^2, using the SHELXL 93 computer program.[22] The scattering factors were taken from Ref. 23. All non-hydrogen atoms were assigned anisotropic thermal parameters. H atoms were also obtained from Fourier maps. Correction for Lorentz and polarization effects were done. The final R factors were $R(F) = 0.037$ [$wR(F^2) = 0.096$]. Maximum and minimum peaks in the final difference synthesis were 0.421 and -0.524 e Å^{-3}, respectively. The final atomic positional parameters are listed in Table 2. All drawings were made using PLATON.[24]

Table 1. Crystal data, details of data collection and structure refinement for the $[Cu(C_{10}H_9N_3)_2(SCN)_2]$ complex.

Formula	$C_{22}H_{18}N_8S_2Cu$
Molecular weight	521.9
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	7.642(2)
b/Å	17.527(3)
c/ Å	8.372(2)
β/°	102.51(2)
V/Å^3	1094.7(4)
Z	4
D_{calc}/g cm^{-3}	1.584
D_{obs}/g cm^{-3}	1.58(1)
Crystal size/mm	0.30 × 0.09 × 0.08
F(000)	534
μ(Mo $K\alpha$)/mm^{-1}	1.218
T/K	298
Radiation, λ(Mo $K\alpha$)/Å	0.71070
Scan type	ω–2θ
θ-Range/°	2.32–29.96
Check reflections	3, −3, −2; 0, −4, −3
No. of measured reflections	3384
Interval h, k, l	$0 < h < 10$, $0 < k < 24$, $-11 < l < 11$
No. of variables	179
No. of unique reflections with $F_o > 4\sigma(F_o)$	2279
$R(F) = [\Sigma(\lvert F_o\rvert - \lvert F_c\rvert)]/\Sigma\lvert F_o\rvert$	0.037
$wR(F^2) = \{\Sigma[w\lvert F_o\rvert^2 - \lvert F_c\rvert^2)^2]\}/\Sigma[w(\lvert F_o\rvert^2)^2]^{1/2}$	0.096
$w = 1/[\sigma^2\lvert F_o\rvert^2 + (0.0584p)^2 + 0p]$	
$p = [\lvert F_o\rvert^2 + 2\lvert F_c\rvert^2]/3$	
Goodness-of-fit	1.050

Results and discussion

Figure 1 shows a perspective view of the $[Cu(dpa)_2(SCN)_2]$ complex, with detailed labelling of the atoms. Bond distances and angles are given in Table 3.

The structure of the title compound consists of isolated $[Cu(dpa)_2(SCN)_2]$ molecules. The complex is formed by two 2,2′-dipyridylamine molecules and two *S*-thiocyanate anions bonded to a copper(II) cation (Fig. 1). The coordination sphere around the Cu^{2+} ion can be described as distorted elongated tetragonal octahedral. The equatorial positions are occupied by the N(1) and N(2) nitrogen atoms from two molecules of the 2,2′-dipyridylamine ligand [Cu–N(1), N(2); 2.006(2) × 2 and 2.024(2) × 2 Å, respectively]. In the axial sites the S(1) atoms, belonging to the thiocyanate anions, are placed with distances Cu–S(1) of 2.929(1) × 2 Å. These distances are similar to those reported for related *S*-thiocyanate copper(II) complexes.[25–27] The angles S_{axial}–Cu–$N_{equatorial}$ range from 83.98(5) to 96.02(5)°. The four equatorial atoms are practically coplanar, and the copper(II) ions are placed on the plane formed by the coordinated nitrogen atoms of the dpa ligand. The 2,2′-dipyridylamine molecule may be considered as non-planar because the value of the dihedral angle between the pyridine rings is 42.0(1)°. As expected, the NCS groups are practically linear. The values of the C–S and C–N bond lengths and the Cu–S(1)–C(11) bond angle

Table 2. Fractional atomic coordinates and equivalent isotropic thermal parameters for $[Cu(C_{10}H_9N_3)_2(SCN)_2]$ (e.s.d.s in parentheses).

Atom	x/a	y/b	z/c	U_{eq}/Å$^{2\,a}$
Cu	0	0	0	28(1)
N(1)	−0.0892(2)	0.0083(1)	0.2077(2)	26(1)
N(2)	0.1545(2)	−0.0870(1)	0.1101(2)	27(1)
N(3)	−0.0721(2)	−0.1245(1)	0.2450(2)	29(1)
N(4)	−0.1836(4)	−0.2446(2)	0.0964(4)	63(1)
S(1)	−0.3052(1)	−0.0948(1)	−0.1556(1)	44(1)
C(1)	−0.1269(3)	0.0776(1)	0.2653(3)	31(1)
C(2)	−0.2171(3)	0.0860(1)	0.3875(3)	37(1)
C(3)	−0.2723(3)	0.0207(2)	0.4579(3)	38(1)
C(4)	−0.2290(3)	−0.0494(1)	0.4073(3)	33(1)
C(5)	−0.1313(3)	−0.0539(1)	0.2840(2)	25(1)
C(6)	0.0883(3)	−0.1382(1)	0.2010(2)	26(1)
C(7)	0.1815(1)	−0.2053(1)	0.2579(3)	35(1)
C(8)	0.3489(3)	−0.2167(1)	0.2284(3)	40(1)
C(9)	0.4224(3)	−0.1620(2)	0.1414(3)	39(1)
C(10)	0.3220(2)	−0.0993(1)	0.0863(3)	33(1)
C(11)	−0.2334(3)	−0.1829(1)	−0.1216(3)	38(1)

[a] $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

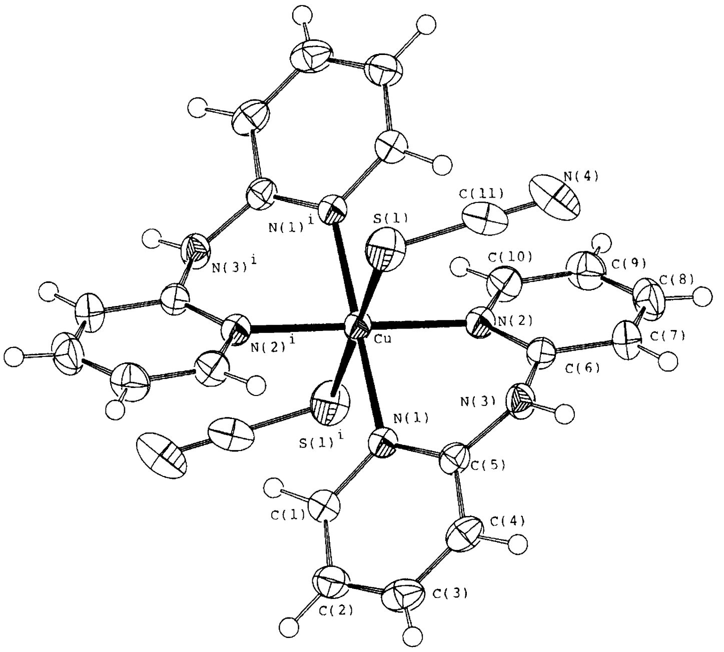

Fig. 1. Molecular structure of the $[Cu(C_{10}H_9N_3)_2(SCN)_2]$ complex.

Table 3. Selected bond distances (in Å) and angles (in °) for $[Cu(C_{10}H_9N_3)_2(SCN)_2]$ (e.s.d.s in parentheses).

Bond distances			
Cu-N(1)	2.006(2) × 2	Cu-N(2)	2.024(2) × 2
Cu-S(1)	2.929(1) × 2	N(1)-C(1)	1.360(3)
N(1)-C(5)	1.338(3)	N(3)-C(5)	1.381(3)
N(3)-C(6)	1.357(3)	N(2)-C(10)	1.355(3)
N(2)-C(6)	1.344(3)	S(1)-C(11)	1.643(2)
C(11)-N(4)	1.151(4)		
Bond angles			
S(1)-Cu-N(1)	92.25(5)	S(1)-Cu-N(2)	96.02(5)
S(1)-Cu-N(1)^i	87.75(5)	S(1)-Cu-N(2)^i	83.98(5)
N(1)-Cu-N(2)	86.22(7)	N(1)-Cu-N(2)^i	93.78(7)
S(1)-Cu-S(1)^i	180.0(6)	N(1)-Cu-N(1)^i	180.0(3)
N(2)-Cu-N(2)^i	180.0(5)	Cu-N(1)-C(1)	120.0(6)
Cu-N(1)-C(5)	121.1(1)	N(1)-C(5)-N(3)	119.5(2)
C(4)-C(5)-N(3)	118.6(2)	C(5)-N(3)-C(6)	125.2(2)
N(3)-C(6)-N(2)	120.1(2)	N(3)-C(6)-C(7)	118.1(2)
Cu-N(2)-C(6)	120.4(1)	Cu-N(2)-C(10)	122.0(1)
Cu-S(1)-C(11)	104.61(8)	S(1)-C(11)-N(4)	179.4(3)

Symmetry code: i = $-x$, $-y$, $-z$.

are similar to those found in other *S*-thiocyanate complexes.[25–27] The value of the copper–copper intermolecular bond distances ranges from 7.6(1) to 9.7(1) Å. The distortion of the coordination polyhedron from an octahedron ($\Delta = 0$) to a trigonal prism ($\Delta = 1$) has been examined using the description of Muetterties and Guggenberger.[28,29] The value obtained, $\Delta = 0.15$, indicates that the $[CuN_4S_2]$ polyhedron is close to octahedral geometry.

The interest in the IR spectrum of the complex lies mainly in the bands due to the NCS group. A first feature is the existence of one band corresponding to the stretching modes of the CN and CS groups, in accordance with the existence of two thiocyanate anions crystallographic equivalents. The ν(CN) and ν(CS) stretching vibrations appear at 2065 and 665 cm^{-1}, respectively. The band corresponding to the bending mode, δ(SCN), is detected at 435 cm^{-1}. The positions of these bands are in the range generally found for thiocyanate anions coordinated to the metallic cations by the sulfur atom.[30]

The reflectance electronic spectrum exhibits three bands in the visible region at frequencies 11 495, 15 505 and 17 860 cm^{-1}. These bands can be assigned as the transitions to x^2-y^2 ($^2B_{1g}$) level from z^2 ($^2A_{1g}$); xy ($^2B_{2g}$) and xz, yz (^2E_g) components, respectively, for a hexacoordinated copper(II) complex with a tetragonally elongated distortion (ideal symmetry, D_{4h}).[31] A charge-transfer band with a maximum at approximately 24 390 cm^{-1} can be also observed in the electronic spectrum.

The Q- and X-band ESR powdered spectra of the complex are shown in Fig. 2. The Q-band ESR spectrum exhibits an axial resolution of the g tensor in parallel and perpendicular components ($g_{\parallel}=2.237$, $g_{\perp}=2.055$, $\langle g \rangle = 2.116$), with no significant variation from room temperature to 4.2 K. The X-band ESR powder spectrum shows the signal corresponding to the $\Delta M_s = \pm 1$ followed transition (≈3200 G), together with a weak absorption approximately at a half-field value of the mean signal, which corresponds to the $\Delta M_s = \pm 2$ forbidden transition. This feature indicates the existence of interactions between pairs of Cu^{II} ions. The interspin distance (r) (in Å) can be calculated by using the expression of Eaton *et al.*:[32,33] relative intensity = (intensity of $\Delta M_s = \pm 2$)/(total intensity of $\Delta M_s = \pm 1$) $= Ar^{-6}$ $(9.1/\nu^2)$, where ν is the spectrometer operating frequency in GHz and $A = 21 \pm 2$ is a calculated parameter. From the X-band ESR spectrum in Fig. 2, we obtain $r = 8.2$ Å. This value is in good agreement with the mean distance crystallographically determined for copper(II) ions from different $[Cu(dpa)_2(SCN)_2]$ molecules in the unit cell, 8.6(9) Å. Taking into account the structure of the complex three mechanisms of interaction can be proposed: (i) a dipolar interaction between copper(II) centres at a minimum distance of 7.6(1) Å (similar situations have been observed in other systems);[33] (ii) a dipolar interaction through sulfur atoms of the thiocyanate anions belonging to different molecules at a minimum distance of 5.5(1) Å; (iii) a superexchange pathway which involves a π–π interaction between pyridine rings of the 2,2′-dipyridylamine ligand, along the [101] direction with a minimum distance of 3.4(1) Å. The last mechanism seems to be the most reasonable, considering the large distances observed in the two first cases.

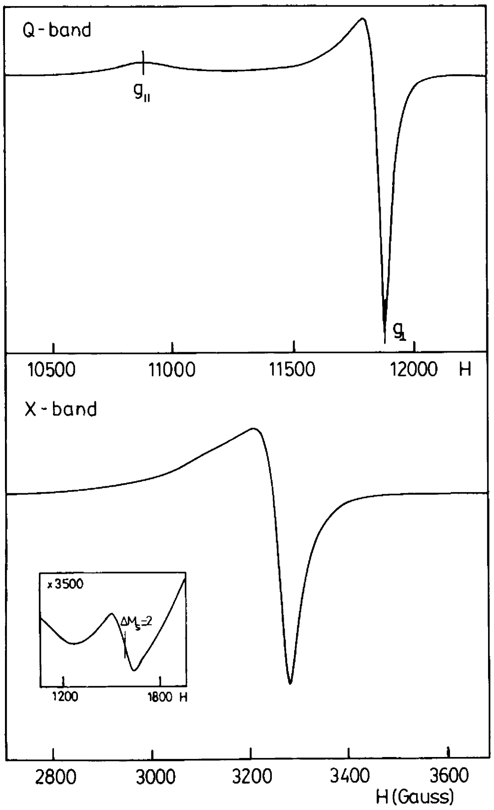

Fig. 2. Q- and X-band ESR spectra of $[Cu(C_{10}H_9N_3)_2(SCN)_2]$ at 4.2 K.

The covalence factor (K) has been calculated from the ESR and reflectance measurements,[34,35] by using the following expressions in D_{4h} symmetry:

$$g_{\parallel} = g_0 - [(8K_{\parallel}{}^2\lambda_0)/\Delta_{\parallel}]$$

$$g_{\perp} = g_0 - [(2K_{\perp}{}^2\lambda_0)/\Delta_{\perp}]$$

where $\Delta_{\parallel} = E(^2B_{2g}) - E(^2B_{1g})$ and $\Delta_{\perp} = E(^2E_g) - E(^2B_{1g})$, $g_0 = 2.0023$ and $\lambda_0 = -830$ cm^{-1} for the Cu^{II} ion. The values obtained, $K_{\parallel} = 0.74$ and $K_{\perp} = 0.75$, are similar to those found in related complexes.[36]

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