

Short Communication

Crystal and Molecular Structure of Tris(1,10-phenanthroline)copper(II) Trifluoromethylsulfonate Monohydrate

Jorunn Sletten^{*a} and Miguel Julve^b

^aDepartment of Chemistry, University of Bergen, Allégaten 41, N-5007 Bergen, Norway and ^bDepartment of Inorganic Chemistry, University of Valencia, Dr. Moliner 50, 46100 Burjassot, Valencia, Spain

Sletten, J. and Julve, M., 1999. Crystal and Molecular Structure of Tris(1,10-phenanthroline)copper(II) Trifluoromethylsulfonate Monohydrate. – Acta Chem. Scand. 53: 631–633. © Acta Chemica Scandinavica 1999.

Crystal structures of three salts containing the $[\text{Cu}(\text{phen})_3]^{2+}$ complex ion have previously been reported (phen = 1,10-phenanthroline): $[\text{Cu}(\text{phen})_3](\text{ClO}_4)_2$,¹ $[\text{Cu}(\text{phen})_3](\text{S}_4\text{O}_6) \cdot 5\text{H}_2\text{O}$ ² and $[\text{Cu}(\text{phen})_3](\text{TCNQ})_2 \cdot 0.5\text{CH}_3\text{OH}$.³ The copper coordination geometry encountered in the last compound differs somewhat from that observed in the other two. In the course of our work on dinuclear copper(II) complexes we have isolated a fourth salt of the $[\text{Cu}(\text{phen})_3]^{2+}$ family, and we hereby report the crystal structure of the mononuclear complex $[\text{Cu}(\text{phen})_3](\text{tf})_2 \cdot \text{H}_2\text{O}$ (tf = trifluoromethylsulfonate = triflate).

Experimental

Preparation of compound. The compound was originally obtained as a side product during work aimed at synthesizing a dinuclear hydroxo-bridged copper(II) complex with phenanthroline as terminal ligands. Subsequently, the following more rational procedure was utilized: An ethanolic solution of 1.5 mmol (0.27 g) phen was added to an aqueous solution of 0.5 mmol (0.18 g) $\text{Cu}(\text{CF}_3\text{SO}_3)_2$. The solution was stirred for 15 min at approximately 40 °C, and then evaporated to dryness. Recrystallisation from ethanol afforded prismatic, light blue polyhedral crystals of X-ray quality.

Spectroscopy. The IR spectrum was recorded with a Perkin–Elmer 1750 spectrophotometer as KBr pellets in the 4000–400 cm^{-1} region. The X-band EPR spectrum on a polycrystalline sample was measured with a Bruker ER 200D spectrometer at room temperature.

X-Ray diffraction study. Diffraction data were collected at 293 K with a 2K SMART CCD area detector diffractometer using ω rotation scans and a scan width of 0.3°. Crystal parameters and refinement results are listed in Table 1. A total of 30 923 reflections were measured within 2θ of 50.0°, of these 6684 were independ-

Table 1. Crystal data and structure refinement for $[\text{Cu}(\text{phen})_3](\text{CF}_3\text{SO}_3)_2 \cdot \text{H}_2\text{O}$.

Empirical formula	$\text{C}_{38}\text{H}_{26}\text{CuF}_6\text{N}_6\text{O}_7\text{S}_2$
Formula weight	920.31
Temperature/K	293(2)
Wavelength/Å	0.71073
Space group	$P\bar{1}$
$a/\text{Å}$	10.7448(3)
$b/\text{Å}$	13.4992(3)
$c/\text{Å}$	14.8755(4)
$\alpha/^\circ$	104.1650(10)
$\beta/^\circ$	104.2840(10)
$\gamma/^\circ$	105.7230(10)
$V/\text{Å}^3$	1897.10(8)
Z	2
$D_{\text{calc}}/\text{g cm}^{-3}$	1.611
μ/mm^{-1}	0.775
Crystal size/mm	0.57 × 0.45 × 0.30
$\theta_{\text{max}}/^\circ$	25.0
Reflections collected	30 923
Unique reflections	6684 [$R(\text{int}) = 0.0261$]
Data/restraints/parameters	6672/0/542
S , Goodness-of-fit on F^2	1.046
R_1 ($I > 2\sigma$, 6036 refl.)	0.0497
wR_2 ($I > 2\sigma$, 6036 refl.)	0.1494
R_1 (all data, 6684 refl.)	0.0538
wR_2 (all data, 6684 refl.)	0.1547
Extinction coefficient	0.0070(11)

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; \quad wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}; \\ S = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{(n-p)} \right\}^{1/2}; \quad w = 1/\sigma^2(F_o^2) + (0.0971P)^2 \\ + 1.85P, \text{ where } P = [(\text{maximum of } 0 \text{ or } F_o^2) + 2F_c^2]/3.$$

* To whom correspondence should be addressed.

ent. An empirical absorption correction was carried out (SADABS).⁴ The structure was solved by direct methods and refined by full-matrix least-squares refinement, based on F^2 and including all reflections. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms attached to carbon were included at idealized positions while hydrogen atoms of the water molecule were located in a difference Fourier map; all hydrogen parameters were adjusted according to the riding model. The residual electron density as well as the thermal parameters suggest that one of the triflate ions may be disordered, the highest peaks in the difference map all being in the vicinity of atoms belonging to this ion. No reasonable disordered model could be refined, however. Residual electron density in regions apart from the triflate ions are below $0.36 \text{ e } \text{Å}^{-3}$. The refinement converged at a conventional R -factor of 0.0497 (for 6036 reflections with $I > 2\sigma$).

For data collection and data integration the SMART and SAINT programs were used.⁵ All other calculations were performed with the SHELXTL programs.⁴ Coordinates of non-hydrogen atoms are listed in Table 2, selected bond distances and angles in Table 3.

Results and discussion

The structure consists of $[\text{Cu}(\text{phen})_3]^{2+}$ cations (Fig. 1) and non-coordinated CF_3SO_3^- ions. One of the phenanthroline groups is bound to copper in an approximately symmetrical fashion [Cu–N of 2.043(2) and 2.079(3) Å], while the two other groups are clearly asymmetrically coordinated [Cu–N 2.012(3), 2.324(3) Å and 2.054(3), 2.367(3) Å, respectively], creating an elongated octahedral copper coordination geometry (the average Cu–N equatorial and axial distances being 2.047 and 2.346 Å, respectively). Rather similar coordination geometries were observed in two of the previously described tris(1,10-phenanthroline)copper(II) structures, $[\text{Cu}(\text{phen})_3](\text{ClO}_4)_2$ and $[\text{Cu}(\text{phen})_3](\text{S}_4\text{O}_6) \cdot 5\text{H}_2\text{O}$,^{1,2} where the corresponding distances are 2.04, 2.33 and 2.056, 2.311 Å, respectively. In $[\text{Cu}(\text{phen})_3](\text{TCNQ})_2 \cdot 0.5\text{CH}_3\text{OH}$,³ on the other hand, the distortion is significantly different with the Cu–N distances more evenly distributed from 2.04 to 2.27 Å. In this latter case a long, an intermediate and a short axis may be identified, the average Cu–N bond lengths being 2.23, 2.12 and 2.05 Å, respectively. The N–Cu–N bond angles for the long axis deviate from linearity by 4.2° in the present compound, which may be compared to the 0.8 and 6.1° found in the perchlorate and tetrathionate salts; in the TCNQ the corresponding value is 14.3° . The difference in distortion is also reflected in the dihedral angles between the phenanthroline rings: while in tetrathionate, perchlorate and triflate salts average deviations from orthogonality are from 2.5 to 7.4° , in the TCNQ salt the corresponding value is 12.5° . The differences in geometries of the $\text{Cu}(\text{phen})_3^+$ cations may be related to differences in crystalline environment. In the TCNQ salt a distinct

Table 2. Atomic coordinates ($\times 10^4$) for $[\text{Cu}(\text{phen})_3](\text{CF}_3\text{SO}_3)_2 \cdot \text{H}_2\text{O}$.

Atom	x	y	z
Cu	5816(1)	2218(1)	3039(1)
S(1)	–1306(1)	–3015(1)	–64(1)
S(2)	1755(1)	3164(1)	4972(1)
F(1)	1283(3)	–2406(5)	968(4)
F(2)	330(5)	–1272(3)	1400(3)
F(3)	–81(4)	–2730(4)	1777(2)
F(4)	266(5)	1784(4)	5557(3)
F(5)	2423(5)	2310(4)	6318(3)
F(6)	1353(5)	3317(4)	6622(3)
O(1)	–2433(3)	–2834(3)	211(3)
O(2)	–895(3)	–2454(3)	–699(2)
O(3)	–1364(4)	–4125(3)	–320(3)
O(4)	3018(5)	3974(6)	5400(4)
O(5)	1735(5)	2259(4)	4207(3)
O(6)	555(4)	3420(4)	4600(3)
O(7)	–335(5)	–1442(4)	–2093(3)
N(1)	6689(3)	1054(2)	2793(2)
N(2)	4413(3)	1179(2)	1672(2)
N(3)	5074(3)	3430(2)	2995(2)
N(4)	7277(3)	3297(2)	2453(2)
N(5)	4343(3)	1239(2)	3723(2)
N(6)	6842(3)	2887(2)	4529(2)
C(1)	7886(3)	1053(3)	3321(3)
C(2)	8356(4)	189(3)	3059(3)
C(3)	7550(4)	–705(3)	2239(3)
C(4)	6294(3)	–729(3)	1664(2)
C(5)	5383(4)	–1616(3)	790(3)
C(6)	4195(4)	–1573(3)	252(3)
C(7)	3797(3)	–640(3)	523(2)
C(8)	2597(4)	–538(3)	–20(3)
C(9)	2333(4)	399(3)	286(3)
C(10)	3267(3)	1250(3)	1134(2)
C(11)	4673(3)	244(2)	1372(2)
C(12)	5914(3)	188(2)	1962(2)
C(13)	4103(4)	3572(3)	3351(3)
C(14)	3432(5)	4294(3)	3147(3)
C(15)	3777(4)	4848(3)	2549(3)
C(16)	4835(4)	4745(3)	2173(3)
C(17)	5282(5)	5311(3)	1548(3)
C(18)	6331(5)	5212(3)	1238(3)
C(19)	7063(4)	4544(3)	1539(2)
C(20)	8227(4)	4452(3)	1293(3)
C(21)	8890(4)	3823(3)	1637(3)
C(22)	8378(3)	3248(3)	2217(2)
C(23)	6634(3)	3941(2)	2128(2)
C(24)	5482(3)	4030(2)	2435(2)
C(25)	3115(4)	462(3)	3325(3)
C(26)	2459(4)	–58(3)	3873(3)
C(27)	3082(4)	245(3)	4853(3)
C(28)	4382(4)	1082(3)	5311(3)
C(29)	5114(5)	1473(4)	6348(3)
C(30)	6346(5)	2280(4)	6751(3)
C(31)	6979(4)	2801(3)	6156(2)
C(32)	8239(4)	3669(3)	6539(3)
C(33)	8753(4)	4143(3)	5931(3)
C(34)	8020(4)	3728(3)	4928(3)
C(35)	6294(3)	2426(2)	5133(2)
C(36)	4976(3)	1562(3)	4703(2)
C(37)	127(5)	–2331(5)	1069(4)
C(38)	1391(5)	2526(5)	5863(3)

Table 3. Selected bond lengths (in Å) and angles (in °) for $[\text{Cu}(\text{phen})_3](\text{CF}_3\text{SO}_3)_2 \cdot \text{H}_2\text{O}$.

Cu–N(3)	2.012(3)	C(8)–C(9)	1.365(5)
Cu–N(1)	2.043(2)	C(9)–C(10)	1.399(5)
Cu–N(6)	2.054(3)	C(11)–C(12)	1.436(4)
Cu–N(2)	2.079(3)	C(13)–C(14)	1.407(5)
Cu–N(4)	2.324(3)	C(14)–C(15)	1.351(6)
Cu–N(5)	2.367(3)	C(15)–C(16)	1.410(6)
N(1)–C(1)	1.331(4)	C(16)–C(24)	1.406(5)
N(1)–C(12)	1.358(4)	C(16)–C(17)	1.432(5)
N(2)–C(10)	1.335(4)	C(17)–C(18)	1.344(6)
N(2)–C(11)	1.359(4)	C(18)–C(19)	1.428(6)
N(3)–C(13)	1.318(4)	C(19)–C(23)	1.409(4)
N(3)–C(24)	1.364(4)	C(19)–C(20)	1.415(5)
N(4)–C(22)	1.328(4)	C(20)–C(21)	1.360(6)
N(4)–C(23)	1.354(4)	C(21)–C(22)	1.407(5)
N(5)–C(25)	1.323(4)	C(23)–C(24)	1.445(5)
N(5)–C(36)	1.348(4)	C(25)–C(26)	1.395(5)
N(6)–C(34)	1.328(4)	C(26)–C(27)	1.349(6)
N(6)–C(35)	1.370(4)	C(27)–C(28)	1.411(6)
C(1)–C(2)	1.401(5)	C(28)–C(36)	1.412(4)
C(2)–C(3)	1.373(5)	C(28)–C(29)	1.433(6)
C(3)–C(4)	1.396(5)	C(29)–C(30)	1.343(6)
C(4)–C(12)	1.411(4)	C(30)–C(31)	1.443(5)
C(4)–C(5)	1.435(5)	C(31)–C(32)	1.401(5)
C(5)–C(6)	1.354(6)	C(31)–C(35)	1.408(5)
C(6)–C(7)	1.436(5)	C(32)–C(33)	1.368(6)
C(7)–C(11)	1.404(4)	C(33)–C(34)	1.390(5)
C(7)–C(8)	1.404(5)	C(35)–C(36)	1.438(5)
N(3)–Cu–N(1)	165.86(10)	N(6)–Cu–N(4)	101.15(10)
N(3)–Cu–N(6)	93.59(10)	N(2)–Cu–N(4)	96.60(9)
N(1)–Cu–N(6)	96.00(10)	N(3)–Cu–N(5)	99.75(10)
N(3)–Cu–N(2)	93.14(10)	N(1)–Cu–N(5)	92.66(9)
N(1)–Cu–N(2)	80.80(10)	N(6)–Cu–N(5)	75.98(10)
N(6)–Cu–N(2)	162.01(10)	N(2)–Cu–N(5)	86.44(10)
N(3)–Cu–N(4)	77.24(10)	N(4)–Cu–N(5)	175.80(9)
N(1)–Cu–N(4)	90.70(9)		

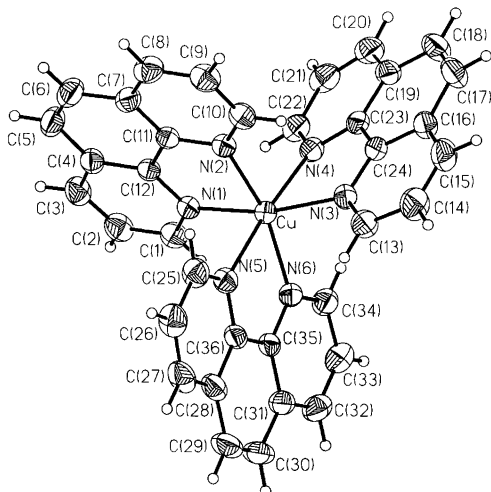


Fig. 1. Atomic numbering in the $[\text{Cu}(\text{phen})_3]^{2+}$ ion. Thermal ellipsoids are plotted at the 40% probability level.

feature in the crystalline packing is the presence of close to parallel TCNQ and phen planes, resulting in stacks of phen–TCNQ–TCNQ–phen and phen–TCNQ–phen

sequences. In the other three structures the anions cannot provide this type of interaction, and a common feature of the crystalline packing is that partial overlap between planes of parallel phen ligands in neighbouring molecules does occur. Bond distances and angles of the phenanthroline moieties in the present structure are similar to those found in the free molecule.⁶ The anions both exhibit a staggered conformation around the S–C bond. Hydrogen bonds occur between the water molecule and the anions [$\text{O} \cdots \text{O}$ of 2.843(5) and 2.905(6) Å].

Besides the bands due to coordinated phenanthroline, the IR spectrum of the copper(II) complex shows features which are consistent with the occurrence of lattice water⁷ and uncoordinated triflate.^{8,9} medium-intensity sharp peaks at 3600 and 3500 cm^{-1} (antisymmetric and symmetric OH stretching) and at 1625 cm^{-1} (HOH bending) from the free water molecule, and a heptuplet of strong (1265, 1150, 1030 and 640 cm^{-1}) and medium intensity (1220, 575 and 520 cm^{-1}) peaks attributed to the vibrational modes of ionic triflate. The occurrence of hydrogen bonds between the water molecule and an oxygen atom of each of the anions is most likely responsible for the slight splitting of the asymmetric SO_3 stretching of the triflate (1280, 1260 and 1250 cm^{-1}).

The X-band EPR spectrum on a polycrystalline sample at room temperature looks like an axial doublet with $g_{\parallel} = 2.27$ and $g_{\perp} = 2.09$, hyperfine coupling being observed on the parallel component. The value of $A_{\parallel}(\text{Cu}) = 125$ G is easily obtained from the uniform signal splitting of three peaks (four peaks were expected, but the fourth one is obscured by the perpendicular signal) which arise from the hyperfine coupling with the copper nucleus ($I = 3/2$). The observed pattern $g_{\parallel} > g_{\perp} > 2.0$ is indicative of a copper(II) $d(x^2 - y^2)$ orbital ground state in agreement with the elongated octahedral copper environment.

References

- Anderson, O. P. *J. Chem. Soc., Dalton Trans.* (1973) 1237.
- Freire, E., Baggio, S., Baggio, R. and Garland, M. T. *Acta Crystallogr., Sect. C* 54 (1998) 464.
- Bencini, A., Midollini, S. and Zanchini, C. *Inorg. Chem.* 28 (1989) 1963.
- SHELXTL-PLUS Version 5.10, Sheldrick, G. M., Bruker AXS, Inc., Madison, WI, 1997.
- SMART, Version 4.0, Data Collection Software; SAINT, Version 4.0, Data Integration Software, Bruker AXS, Inc., Madison, WI 1997.
- Nishigaki, S., Yoshioka, H. and Nakatsu, K. *Acta Crystallogr., Sect. B* 34 (1978) 875.
- Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Edn., Wiley, New York 1986, p. 228 and refs. therein.
- Miles, M. G., Doyle, G., Cooney, R. P. and Tobias, R. S. *Spectrochim. Acta, Part A* 25 (1969) 1515.
- Lawrance, G. A. *Chem. Rev.* 86 (1986) 17.

Received January 18, 1999.