Synthesis, Single-crystal Structure and Raman Spectrum of $Cu[N(CN)_2]_2 \cdot 2\,NH_3$

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Transparent blue crystals of $Cu[N(CN)_2]_2 \cdot 2\,NH_3$ were obtained by blending solutions of $Na[N(CN)_2]$ and $Cu(NO_3)_2 \cdot 2.5\,H_2O$ in aqueous ammonia and subsequent evaporation of the solvent under ambient conditions. $Cu[N(CN)_2]_2 \cdot 2\,NH_3$ crystallizes in space group $P\bar{1}$ (no. 2, $Z = 2$) with the cell parameters $a = 746.1(4)$, $b = 747.8(4)$ and $c = 894.4(5)$ pm, and the angles $\alpha = 68.94(2)$, $\beta = 75.52(1)$ and $\gamma = 68.22(4)^\circ$. The presence of the dicyanamide anion and the ammonia molecules was verified by Raman spectroscopy.

Key words: Copper(II), $[N(CN)_2]_2^-$ Anion, Ammonia, Dicyanamide, Raman Spectrum

Introduction

First-row transition metal dicyanamide ([dca]) compounds are object to intensive research recently, because the [dca] anion has three coordinative nitrogen positions (assigned symbols: μ_1, μ_3 and μ_5 [1]) and is therefore interesting as a building block and/or spacer for tailor-made compounds with potentially interesting magnetic properties (*e. g.* refs. [1 – 4]). While searching the literature, it struck us as strange that many donor molecules were used to crystallize the [dca] containing compounds; even water is incorporated in the crystal structure of $Cu_2[dca]_4 \cdot H_2O$ [5], but there is no report of ammonia in Cu^{2+}-[dca] compounds. Since Cu^{2+} has a strong affinity for ammonia, and Cu^{2+} salts are usually easily dissolved in polar solvents, we tried crystallizing the Cu^{2+}-[dca] salt from concentrated aqueous ammonia. Crystals readily formed by evaporating the solvent in air. Here we present as the result of our efforts the single-crystal structure determination and the Raman spectrum of $Cu[dca]_2 \cdot 2\,NH_3$.

Experimental Section

Synthesis

All manipulations were performed under normal atmospheric conditions. $Cu[dca]_2 \cdot 2\,NH_3$ was synthesized by dissolving 0.27 g (3 mmol) Na[dca] (96 %, powder, Alfa Aesar) and 0.7 g (3 mmol) $Cu(NO_3)_2 \cdot 2.5\,H_2O$ (Sigma Aldrich, ACS Grade 98 %) in 1 mL of deionized water each. Upon mixing these solutions, a green slurry instantly formed. By adding 10 mL of 25 % NH_3(aq), the slurry transformed into a deep-blue, transparent solution. After eight hours of evaporation under normal atmospheric conditions, blade-like, deep-blue crystals of $Cu[dca]_2 \cdot 2\,NH_3$ formed, while the remaining solution was nearly colorless and transparent. $Cu[dca]_2 \cdot 2\,NH_3$ loses the solvate molecules and its crystallinity after a few days when not either kept in its mother liquor or if not protected by a viscous liquid, such as polybutene. The title compound does not form when diluted solutions of the Cu salts or of NH_3 are used; in that case $Cu[dca]_2$ [1] preferably forms.

Crystallographic studies

Samples of the crystalline product were immersed in polybutene oil (Aldrich, M_n ∼320, isobutylene > 90 %) for single-crystal selection under a polarization microscope, mounted in a drop of polybutene sustained in a plastic loop, and placed onto the goniometer. A cold stream of nitrogen ($T = 170(2)$ K) froze the polybutene oil, thus keeping the crystal stationary and protected from oxygen and moisture in the air. Intensity data were collected with a Bruker X8 Apex II diffractometer equipped with a 4 K CCD detector and graphite-monochromatized MoK_α radiation ($\lambda = 71.073$ pm). The intensity data were manipulated with the program package [6] that came with the diffractometer. An empirical absorption correction was applied using SADABS [7]. The intensity data were evaluated, and the input files for solving and refining the crystal structure were prepared by XPREP [8]. The program SHELXS-97 [9, 10] found the positions of Cu, C and N with the help of Direct Methods techniques. The positions of the hydrogen atoms were apparent from the positions of highest electron density on the difference Fourier map resulting from the first refinement cycles by full-matrix least-squares calculations on F^2 in SHELXL-97 [11, 12]. Doing further refinement cycles with all atoms being refined unrestained, the refinement converged and resulted in a stable model for the crystal structure.

Table 1. Summary of single-crystal X-ray diffraction structure determination data of $Cu[dca]_2 \cdot 2\ NH_3$.

Compound	$Cu[dca]_2 \cdot 2\ NH_3$
M_r	229.71
Crystal color	transparent blue
Crystal shape	elongated plate
Crystal size, mm^3	$0.15 \times 0.10 \times 0.02$
Crystal system	triclinic
Space group (no.); Z	$P\bar{1}$ (2); 2
Lattice parameters	
a, pm	746.1(4)
b, pm	747.8(4)
c, pm	894.4(5)
α, deg	68.94(2)
β, deg	75.52(1)
γ, deg	68.22(1)
V, $Å^3$	428.5(4)
D_{calcd}, g cm^{-3}	1.78
$F(000)$, e^-	230
μ, mm^{-1}	2.5
Diffractometer	Bruker X8 Apex II equipped with a 4 K CCD
Radiation; λ, pm; monochromator	MoK_α; 71.073; graphite
Scan mode; T, K	ϕ- and ω-scans; 170(2)
h, k, l range; $2\theta_{max}$, deg	$-10 \rightarrow 10$, $-9 \rightarrow 10$, $-12 \rightarrow 12$; 58.50
Data correction	LP, SADABS [7]
Transmission: min. / max.	0.648 / 0.746
Reflections: measured / unique	7150 / 2276
R_{int}/R_σ	0.0281 / 0.0372
Unique reflections with $F_o > \sigma(F_o)$	1934
Refined Parameters	143
$R1$[a] / $wR2$[b] / GoF[c] (all refl.)	0.0386 / 0.0613 / 1.028
Factors x / y (weighting scheme)[b]	0.0243 / 0.21
Max. shift / esd, last refinement cycle	< 0.00005
$\Delta\rho_{fin}$ (max, min), e^- $Å^{-3}$	0.41 (75 pm to N2), −0.49 (87 pm to Cu)
CSD number	425 593

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (xP)^2 + yP]^{-1}$, where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$ and x and y are constants adjusted by the program; [c] GoF $= S = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters.

Additional crystallographic details are described in Table 1. Atomic coordinates and equivalent isotropic displacement coefficients are shown in Table 2. Table 3 displays selected interatomic distances and angles of the title compound.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition number CSD–425593 for $Cu[N(CN)_2]_2 \cdot 2\ NH_3$.

Raman spectroscopy

Raman investigations were performed on a microscope laser Raman spectrometer (Jobin Yvon, 1 mW, equipped with an HeNe laser with an excitation line at $\lambda = 632.817$ nm, 50 × magnification, samples in glass capillaries, 8 × 300 s accumulation time) on the very specimen used for the structure determination. The resulting Raman spectrum for $Cu[N(CN)_2]_2 \cdot 2\ NH_3$ is shown in Fig. 1, the exact frequencies and their assigned modes are given in Table 4.

Results and Discussion

Raman spectrum

The frequencies obtained from the Raman spectrum compare well to the vibrational frequencies obtained *e. g.* for $Cu[dca]_2$ [13]. The bands of ammonia were weak, but observed in the typical range [14].

Crystal structure

Each copper atom is coordinated in an octahedral fashion by four dca anions (of which two are crystallographically unique with an end-to-end $\mu_{1,5}$ and

Table 2. Atomic coordinates and equivalent isotropic displacement parameters[a] of $Cu[dca]_2 \cdot 2\,NH_3$.

Atom	Wyckoff site	x	y	z	U_{eq} (pm^2)
Cu	2i	0.29249(3)	0.26798(4)	0.18894(3)	163(1)
N1	2i	0.1565(3)	0.6275(3)	0.1360(2)	237(4)
N2	2i	−0.0962(3)	0.8500(3)	0.2837(2)	273(4)
N3	2i	0.2301(3)	0.2267(3)	0.4288(2)	224(4)
N4	2i	0.3674(3)	0.2692(3)	0.9553(2)	216(4)
N5	2i	0.5666(3)	0.1409(3)	0.7303(2)	278(4)
N6	2i	0.7166(3)	0.3236(3)	0.4694(2)	326(5)
C1	2i	0.0385(3)	0.7229(3)	0.2130(2)	174(4)
C2	2i	0.1597(3)	0.2028(3)	0.5611(3)	197(4)
C3	2i	0.4626(3)	0.2194(3)	0.8445(2)	190(4)
C4	2i	0.6430(3)	0.2468(3)	0.5934(3)	218(4)
NH3A	2i	0.5585(3)	0.2658(3)	0.1926(2)	186(4)
NH3B	2i	0.0322(3)	0.2532(3)	0.1885(2)	202(4)
H1	2i	0.565(3)	0.308(4)	0.266(3)	250(65)
H2	2i	0.603(4)	0.330(4)	0.113(3)	322(77)
H3	2i	0.640(4)	0.138(5)	0.216(3)	473(85)
H4	2i	0.039(4)	0.131(5)	0.211(3)	417(83)
H5	2i	−0.051(4)	0.295(4)	0.252(3)	374(80)
H6	2i	−0.011(4)	0.315(4)	0.094(3)	276(67)

[a] U_{eq} is defined as a third of the orthogonalized U_{ij} tensors.

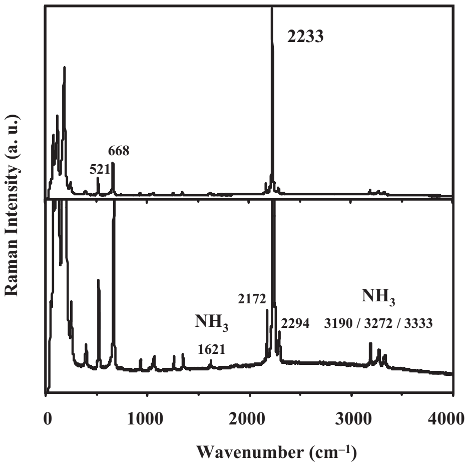

Fig. 1. Raman spectrum of $Cu[dca]_2 \cdot 2\,NH_3$. On the vertical axis, Raman intensities are displayed in arbitrary units. Numbers are given in cm^{-1}. In the lower box, the spectrum is shown with different scaling of the Raman intensity (scaled up 10 times) to emphasize observed Raman modes with low intensities.

Table 3. Selected bond lengths (pm) and angles (deg) of $Cu[dca]_2 \cdot 2\,NH_3$.

Cu–	NH3B	198.7(2)	N1–	C1	115.9(3)
	NH3A	198.7(2)	C1–	N2	131.1(3)
	N3	201.2(2)	N2–	C2	131.4(3)
	N4	202.1(2)	C2–	N3	114.6(3)
	N1	240.5(2)	N4–	C3	115.8(3)
	N5	271.7(4)	C3–	N5	129.9(3)
	$Cu_{(intra)}$	568.9(1)/ 724.9(1)	N5–	C4	131.9(3)
	$Cu_{(inter)}$	523.1(1)	C4–	N6	115.5(3)
NH3A–	H1	84(3)	NH3B–	H4	85(3)
	H2	77(3)		H4	79(3)
	H3	90(3)		H6	88(3)
∠ (N1–C1–N2)		172.8(2)	∠ (N4–C3–N5)		172.6(2)
∠ (C1–N2–C2)		122.3(2)	∠ (C3–N5–C4)		122.3(2)
∠ (N2–C2–N3)		172.0(2)	∠ (N5–C4–N6)		173.7(2)

Table 4. Raman data of $Cu[dca]_2 \cdot 2\,NH_3$ with the assigned vibrational modes. All numbers are given in cm^{-1}.

Assigned modes [13, 14]	$Cu[dca]_2$ [13]	$Cu[dca]_2 \cdot 2\,NH_3$
Lattice vibrations	115 / 210 / 236	81 / 123 / 191
Lattice vibrations	268 /278 / 318	191 / 252
Not assigned		398
γ_s(N–C≡N)	533	521
δ_s(N–C≡N)	655	668
ν_s(N–C)	950	932
Not assigned		1064
Not assigned		1258
ν_{as}(N–C)		1349
δ_{as}(H–N–H) of NH_3		1621
ν_{as}(C≡N)	2174	2172
ν_{as}(N–C) + ν_s(N–C)	2272	2233
ν_s(C≡N)	2294	2294
ν(H–N) of NH_3		3190 / 3272 / 3333

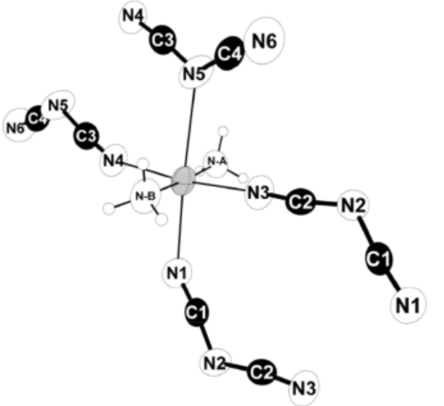

Fig. 2. Coordination sphere of the copper atoms. All atoms are marked with their label assigned in Table 2 except for the hydrogen atoms (white small circles) and the nitrogen atoms of the ammonia molecules (N-A and N-B). The displacement ellipsoids are shown at the 90 % probability level.

a mid-to-end $\mu_{1,3}$ bridging mode, respectively [1]) and two *trans*-bonded ammonia molecules (Fig. 2). All bond lengths and angles are in a familiar range (Table 3), only $d(Cu–\mu_3\text{-}N5) = 271.7(4)$ pm is a little longer than expected if compared to similar compounds, *e. g.* as $Cu[dca]_2$ ($d(Cu–\mu_1\text{-}N) = 198.0(2)$ pm

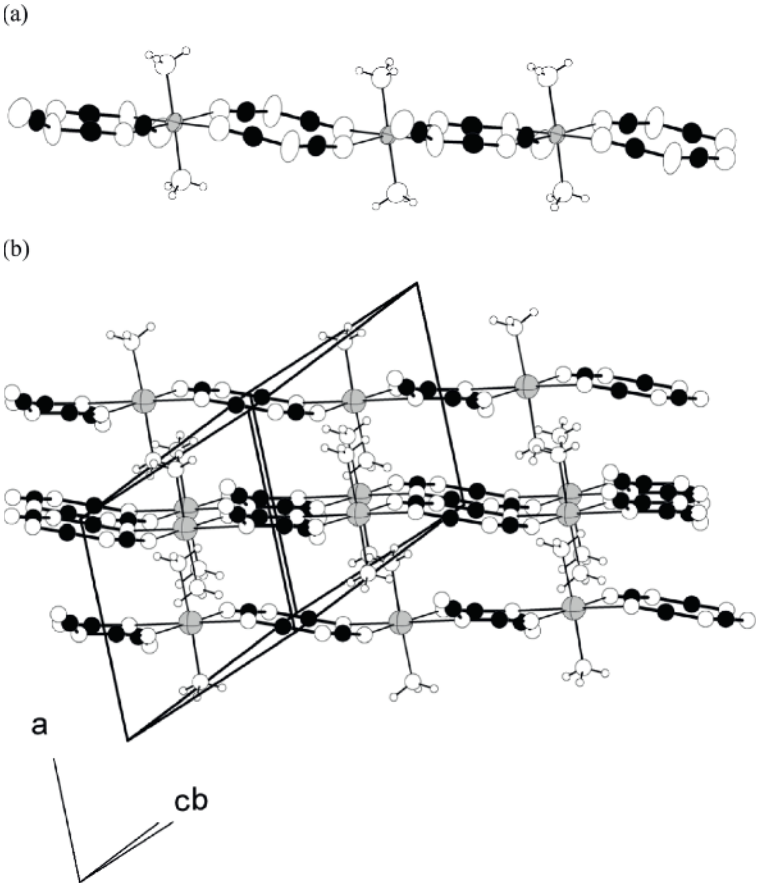

Fig. 3. The quasi-1D chain consisting of the building blocks displayed in Fig. 2 perpendicular to [111]. One type of chain (Fig. 3a) packed together forms the structure (Fig. 3b). The same color code and probability level were used.

$d(\mathrm{Cu}–\mu_3\text{-N}) = 244.9(3)$ pm) [1]. Each dca anion coordinates two Cu cations, therefore, quasi-1-D chains are formed (Fig. 3a). These moieties are packed and held in place only by van der Waals forces, since no specific bonding in between the chains, which are roughly parallel to [111] (Fig. 3), is obvious. The distance between copper cations is quite large (in the chains: 568.9(2) pm; between the chains: 523.1(2) pm, Table 3), therefore only very weak metal-metal bonding or exchange interactions are expected.

Magnetic moments have been measured for Cu[dca]$_2$ [1]. As the found moments were in the expected range, no measurements were done on Cu[N(CN)$_2$]$_2$ · 2 NH$_3$.

Conclusion

The compound Cu[N(CN)$_2$]$_2$ · 2 NH$_3$ was synthesized and characterized by single-crystal X-ray methods and Raman spectroscopy. All structural or spectroscopic results are in the expected range. This Cu(II) compound with a rather simple stoichiometry is one more example of a rather obvious compound waiting to be discovered.

[1] S. R. Batten, K. S. Murray, *Coord. Chem. Rev.* **2003**, *246*, 103 – 130.

[2] M. Kurmoo, C. J. Kepert, *New J. Chem.* **1998**, *2*, 1515 – 1524.

[3] M. Biswas, G. M. Rosair, G. Pilet, S. Mitra, *Inorg. Chim. Acta* **2007**, *360*, 695 – 699.

[4] G. A. van Albada, M. Elba Quiroz-Castro, I. Mutikainen, U. Turpeinen, J. Reedijk, *Inorg. Chim. Acta* **2000**, *298*, 221 – 225.

[5] J. Kožíšek, J. García, Díaz, A. Garcí a Albor, *Acta Crystallogr.* **2007**, *E63*, i125–i126.

[6] APEX2 (version 1.22), SAINT PLUS, Software for the CCD system, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **2004**.

[7] G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen (Germany) **2003**.

[8] XPREP (version 6.14), Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **2003**.

[9] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**.

[10] G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467 – 473.

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

[12] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112 – 122.

[13] A. Ju. Civadze, H. Köhler, *Z. Anorg. Allg. Chem.* **1984**, *510*, 25 – 30.

[14] K. H. Schmidt, A. Müller, *Coord. Chem. Rev.* **1976**, *19*, 41 – 97.