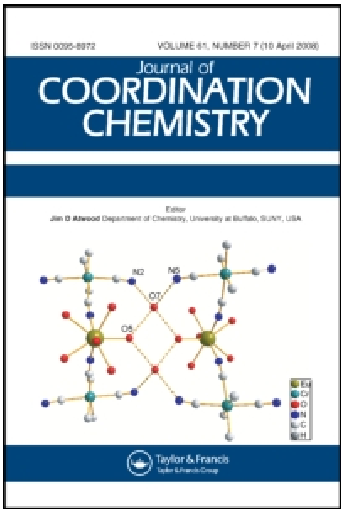

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Synthesis, crystal structure, spectroscopic and magnetic properties of $[Cu(dien)_2][Ni(CN)_4]$

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SYNTHESIS, CRYSTAL STRUCTURE, SPECTROSCOPIC AND MAGNETIC PROPERTIES OF $[Cu(dien)_2][Ni(CN)_4]$

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A new complex, $[Cu(dien)_2][Ni(CN)_4]$ (**1**) [dien = diethylenetriamine] has been obtained by the reaction of $Cu(ClO_4)_2 \cdot 6H_2O$, diethylenetriamine and $K_2[Ni(CN)_4]$ in water, and has been characterized spectroscopically. The crystal structure of **1** has been determined. In the complex, two tridentate dien ligands are bonded to the copper(II) ion in a distorted octahedral arrangement and the $Ni(CN)_4^{2-}$ anion remains outside the coordination sphere.

Keywords: Crystal structure; Tridentate dien ligand; Copper(II); $Ni(CN)_4^{2-}$ anion; Properties

INTRODUCTION

Transition metal cyanide chemistry is an area that has experienced remarkable growth in recent years [1]. Cyanide materials based on the well-known Prussian Blue compound have been revisited in light of their promising properties for an assortment of applications including electronics [2], magnetism [3] and catalysis [4]. The tetracyanonickelate anion, $Ni(CN)_4^{2-}$, is also an ideal building block because it possesses the ability to link various central atoms and thus form molecular, 1D, 2D and 3D structures. Previously 1D structures of $[Ni(en)_2Ni(CN)_4]$ (en = ethylenediamine) [5], $[Ni(en)_2Ni(CN)_4] \cdot 2.16H_2O$ [6], $[Ni(hmtd)Ni(CN)_4] \cdot H_2O$ (hmtd = *N-meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) [7], $[Ni(bpy)_2Ni(CN)_4]$ (bpy = 2,2-bipyridine) [8], $[Ni(pn)_2Ni(CN)_4] \cdot H_2O$ (pn = 1,2-diaminopropane) [9], $[Cu(en)_2Ni(CN)_4]$ [10], $[Ni(TIM)][Ni(CN)]_4$ (TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) [11] and $[NiL][Ni(CN)_4] \cdot 4H_2O$

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(L = 3,10-diethyl-1,3,5,8,10,12-hexaazacyclotetradecane) [12], the 2D structure of $[Cu(NH_3)_2Ni(CN)_4]\cdot 2C_6H_6$ [13] and the molecular structure of the octanuclear complex $[Cu(NH_3)_3Ni(CN)_4]_4$ [14] have been studied. As part of our continuing study in this field [11,12], we report the synthesis, structure, spectroscopic and magnetic properties of a new 'zero-dimensional' complex $[Cu(dien)_2](Ni(CN)_4]$.

EXPERIMENTAL

Materials and Synthesis

All starting reagents were of analytical grade obtained from commercial sources and used without further purification. Cyanide salts are toxic and should be handled with caution! The complex **1** was prepared by reaction of a mixture of $Cu(ClO_4)_2\cdot 6H_2O$ (0.1 mmol), diethylenetriamine (0.2 mmol) and $K_2[Ni(CN)_4]$ (0.1 mmol) in water with stirring. The resulting solution was kept at ambient temperatures for one month to give blue crystals suitable for the X-ray structural analysis. Yield: almost quantitative. *Anal. Calc.* For $C_8H_{17.33}Cu_{0.67}N_{6.67}Ni_{0.67}$ (%): C, 33.28; H, 6.01; N, 32.37. Found: C, 33.29; H, 6.12; N, 32.35. IR (KBr, cm^{-1}): 2125_{ssh}, 2117_{vs} ($\nu_{C\equiv N}$).

Physical Measurements

Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 analyzer. IR spectra (KBr pellets) were recorded on a Shimadzu IR-408 spectrophotometer in the 4000–600 cm^{-1} region. Electronic spectra in water were recorded on a Shimadzu UV-2101PC scanning spectrophotometer. The X-band ESR spectrum on a Bruker ER 200 D-SRC ESR spectrometer was measured at 297 K. Variable temperature susceptibility measurements were carried out with a LDJ 9600 vibrating sample magnetometer in the temperature range 77–300 K at a magnetic field of 5000 G.

X-ray Crystallography

Determination of the unit cell and data collection was performed on a Bruker SMART 1000 diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K with a crystal of size $0.24\times 0.22\times 0.16$ mm. A total of 4189 [R(int) = 0.0625] independent reflections were collected by the ω–2θ scan technique in the range $1.45 \le \theta \le 26.46°$ with index ranges $-18 \le h \le 18$, $-6 \le k \le 11$, $-19 \le l \le 19$. Semiempirical absorption corrections were applied using the SADABS program. The structure of the complex was solved by direct methods and successive difference Fourier syntheses (SHELX-97) and refined by full-matrix least-squares procedure on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97) [15]. Hydrogen atoms were generated geometrically and refined isotropically. The final agreement factor values are $R_1 = 0.0500$, $wR_2 = 0.0932$ ($I > 2\sigma$), $R_1 = \sum(\|F_0 - F_c\|)/\sum|F_0|$, and $wR_2 = (\sum(|F_0|^2 - |F_c|^2)^2/\sum w|F_0|^2)^2$. The weight was $w = 1/[\sigma^2(F_0^2) + (0.0461P)^2 + 1.24P]$ where $P = (F_0^2 + 2F_c^2)/3$. Further details of the structure analysis are given in Table I. Final atomic coordinates for all non-hydrogen atoms and equivalent thermal parameters are listed in Table II. Selected bond lengths and angles are presented in Table III.

TABLE I Data collection and processing parameters for complex (**1**)

Empirical formula	$C_8H_{17.33}Cu_{0.67}N_{6.67}Ni_{0.67}$
Formula weight	288.45
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	$a = 15.167(6)$
	$b = 9.471(4)$
	$c = 15.282(6)$
	$\beta = 111.904(6)$
Volume (Å^3)	2036.8(14)
Z, Calculated density (g cm^{-3})	6, 1.411
Absorption coefficient (mm^{-1})	1.984
$F(000)$	900
θ range for data collection (°)	1.45–26.46
Limiting indices	$-18 \leq h \leq 18$, $-6 \leq k \leq 11$, $-19 \leq l \leq 19$
Reflections collected/unique	11 243/4189 [R(int) = 0.0625]
Completeness to theta = 25.00° (%)	99.5
Absorption correction	Semi-empirical from equivalents
Max., min. transmission	1.000, 0.733
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4189/0/220
Goodness-of-fit on F^2	0.996
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0500$, $wR_2 = 0.0932$
R indices (all data)	$R_1 = 0.1165$, $wR_2 = 0.1198$
Largest diff. peak, hole (e Å^{-3})	0.477, −0.489

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for $[Cu(dien)_2][Ni(CN)_4]$

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
Cu(1)	2579(1)	5658(1)	2943(1)	44(1)
Ni(1)	0	10 000	0	54(1)
Ni(2)	5000	0	5000	41(1)
N(1)	3163(3)	4976(4)	4377(3)	49(1)
N(2)	1848(3)	3749(4)	2788(3)	47(1)
N(3)	1827(3)	5679(5)	1418(3)	57(1)
N(4)	1534(3)	6985(5)	3158(3)	57(1)
N(5)	3318(3)	7558(4)	3144(3)	54(1)
N(6)	3842(3)	4939(4)	2727(3)	54(1)
N(7)	169(4)	8230(8)	1542(5)	127(3)
N(8)	1861(4)	8566(6)	331(3)	78(2)
N(9)	5004(3)	3065(5)	4466(3)	65(1)
N(10)	6659(4)	−441(5)	4397(4)	77(2)
C(1)	2721(4)	3611(6)	4456(4)	57(1)
C(2)	2432(4)	2816(5)	3554(4)	55(1)
C(3)	1586(4)	3260(6)	1813(4)	68(2)
C(4)	1151(4)	4475(7)	1153(4)	72(2)
C(5)	1943(5)	8395(6)	3432(4)	77(2)
C(6)	2613(5)	8707(6)	2944(4)	77(2)
C(7)	3946(4)	7502(6)	2610(4)	70(2)
C(8)	4498(4)	6153(6)	2860(4)	69(2)
C(9)	−106(4)	8900(7)	958(4)	79(2)
C(10)	1149(4)	9124(6)	200(4)	61(2)
C(11)	4983(3)	1905(6)	4656(3)	46(1)
C(12)	6030(4)	−285(5)	4628(4)	50(1)

TABLE III Selected bond length (Å) and angles (°) for the complex

Cu(1)–N(5)	2.081(4)	Cu(1)–N(3)	2.179(4)
Cu(1)–N(2)	2.088(4)	Ni(1)–C(10)	1.850(6)
Cu(1)–N(1)	2.135(4)	Ni(1)–C(9)	1.852(6)
Cu(1)–N(4)	2.142(4)	N(7)–C(9)	1.128(6)
Cu(1)–N(6)	2.171(4)	N(8)–C(10)	1.150(6)
N(5)–Cu(1)–N(2)	178.13(16)	N(1)–Cu(1)–N(3)	162.15(17)
N(5)–Cu(1)–N(1)	96.64(16)	N(4)–Cu(1)–N(3)	92.14(16)
N(2)–Cu(1)–N(1)	81.58(16)	N(6)–Cu(1)–N(3)	88.85(16)
N(5)–Cu(1)–N(4)	81.85(17)	C(10)–Ni(1)–C(10A)	180.0(3)
N(2)–Cu(1)–N(4)	97.66(17)	C(10)–Ni(1)–C(9A)	91.6(2)
N(1)–Cu(1)–N(4)	93.82(15)	C(10A)–Ni(1)–C(9A)	88.4(2)
N(5)–Cu(1)–N(6)	80.61(16)	C(10)–Ni(1)–C(9)	88.4(2)
N(2)–Cu(1)–N(6)	99.95(15)	C(10A)–Ni(1)–C(9)	91.6(2)
N(1)–Cu(1)–N(6)	90.55(15)	C(9A)–Ni(1)–C(9)	180.0(2)
N(4)–Cu(1)–N(6)	162.30(17)	N(2)–Cu(1)–N(3)	80.95(16)
N(5)–Cu(1)–N(3)	100.85(16)		

Crystal Data $C_8H_{17.33}Cu_{0.67}N_{6.67}Ni_{0.67}$, $M = 288.45$, monoclinic, $P2_1/c$, $a = 15.167(6)$, $b = 9.471(4)$, $c = 15.282(6)$ Å, $\beta = 111.906(6)°$, $V = 2036.8(14)$ Å^3, $Z = 6$, $D_c = 1.411\,\mathrm{g\,cm^{-3}}$, μ (Mo Kα) $= 1.984\,\mathrm{mm^{-1}}$, $F(000) = 900$.

RESULTS AND DISCUSSION

Description of the Structure of [Cu(dien)$_2$][Ni(CN)$_4$]

A perspective view of the complex [Cu(dien)$_2$][Ni(CN)$_4$] with the atom labelling scheme is shown in Fig. 1. The crystal structure consists of [Cu(dien)$_2$]$^{2+}$ cations and [Ni(CN)$_4$]$^{2-}$ anions. The coordination sphere around the Cu(II) ion consists of two tridentate dien ligands with *meridonal* configuration. The [Ni(CN)$_4$]$^{2-}$ anions remain outside the coordination sphere. In the complex, the Cu(II) ions, lying on symmetry centres, present a tetragonally elongated distorted octahedral environment. N(1), N(2), N(4) and N(5) atoms of the dien ligands occupy equatorial sites. Axial coordination sites are occupied by N(3) and N(6) atoms of the triamine molecules. The equatorial Cu–N distances 2.081(4) Å (Cu(1)–N(5)), 2.088(4) Å (Cu(1)–N(2)), 2.135(4) Å (Cu(1)–N(1)) and 2.142(4) Å (Cu(1)–N(4)) are slightly longer than those determined for related Cu-dien compounds [16–18]. The complex shows the preference of copper(II) to form a tetragonally distorted octahedron with four strong equatorial bonds and two weaker, longer axial bonds. In complex **1**, all coordination bond angles are far from those of a regular octahedron; the presence of the chelate rings demands N–Cu–N angles that differ from 90° [19]. The large deviation of the axial N–Cu–N angles in complex **1** is dictated by the steric requirements of the dien ligand. Unusually, the [Ni(CN)$_4$]$^{2-}$ anions are not coordinated to Cu(II) ions.

Spectroscopic and Magnetic Properties

IR spectra of **1** (solid) show two sharp $\nu_{C\equiv N}$ bands at 2125 and 2117 cm^{-1} [20]. There are several close peaks in the region 3465–3200 cm^{-1} which may be attributed to N–H vibrations of the dien NH$_2$ groups [21]. Splitting and broadening of these peaks suggest that the NH$_2$ groups are coordinated [21]. The weak bands at 456–453 cm^{-1} may be assigned to Cu–N (dien) vibrations. Electronic spectra of the complex **1** show three

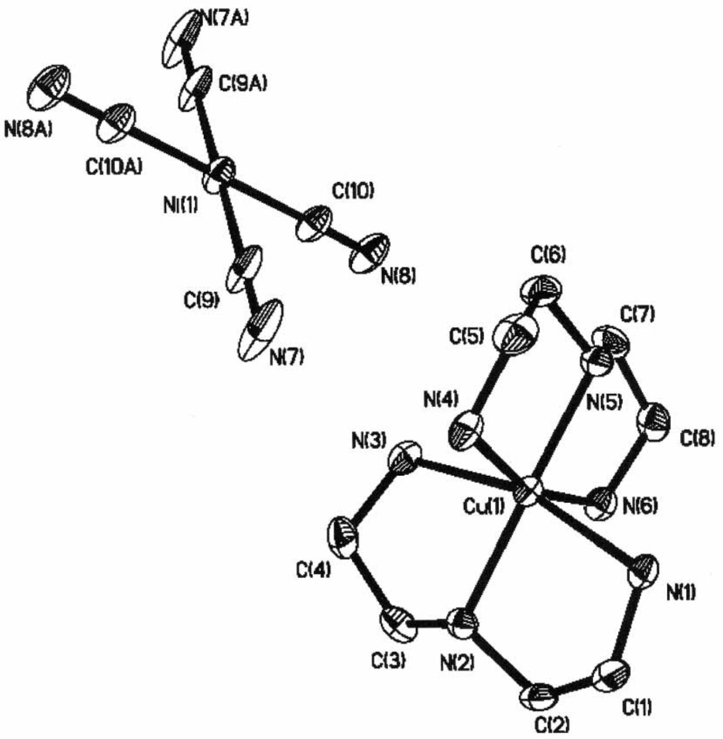

FIGURE 1 Perspective view of the complex $[Cu(dien)_2][Ni(CN)_4]$ (**1**) with H atoms omitted for clarity.

main transitions [22]; a weak band observed around 540 nm ($\varepsilon = 43.76\,cm^{-1}\,M^{-1}$) may be assigned to d–d transitions of the copper(II) ion, a moderately intense band around 315 nm ($\varepsilon = 1313$) is due to ligand-to-metal charge transfer, and the strong band observed around 270 nm ($\varepsilon = 5018$) is due to an intraligand transition [23].

The polycrystalline X-band ESR spectrum of complex **1** at 110 K is axial. ESR parameters for complex 1 are $g_{\|} = 2.15$ and $g_{\perp} = 2.01$. The value of $g_{\|}$ is larger than that of $g_{\perp}$, indicating a tetragonally elongated distorted octahedral environment around the copper(II) ion and a single electron sited in an essentially $d_{x^2-y^2}$ orbital.

As for magnetic properties, the effective magnetic moment of complex **1** is 1.78 BM at room temperature, slightly higher than that of the spin-only value. Upon cooling to 77 K, the μ_{eff} value decreases to 1.60 BM, suggesting a weak antiferromagnetic interaction between Cu(II) ions.

Acknowledgements

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Supplementary Material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centra, CCDC No 228067. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] K.R. Dunbar and R.A. Heintz, *Prog. Inorg. Chem.* **45**, 282 (1997).
[2] Z.Z. Gu, O. Sato, T. Tyoda, K. Hashimoto and A. Fujishima, *Chem. Mater.* **9**, 1092 (1997).
[3] J.S. Miller and A.J. Epstein (Eds.), *MRS Bull.* **21** (2000).
[4] L. Yet, *Angew. Chem. Int. Ed. Engl.* **40**, 875 (2001).
[5] J. Černák, J. Chomič, D. Baloghová and M. Dunaj-Jurčo, *Acta Cryst. C* **44**, 1902 (1988).
[6] J. Černák, J. Chomič, P. Domiano, O. Ori and G.D. Andreeti, *Acta Cryst. C* **46**, 2103 (1990).
[7] G.J. Gainsford and N.F. Curtis, *Aust. J. Chem.* **37**, 1799 (1984).
[8] J. Černák and K.A. Abboud, *Acta Cryst., C* **56**, 783 (2000).
[9] S.Z. Zhan, D. Guo, X.Y. Zhang, C.X. Du and Y. Zhu, *Inorg. Chim. Acta* **298**, 57 (2000).
[10] M. Dunaj-Jurčo, J. Garaj, J. Chomič, V. Haluska and F. Valach, Proceedings of the 6th Conference on Coordination Chemistry, Smolenice-Bratislava, p. 45 (1976).
[11] H.Z. Kou, D.Z. Liao, Z.H. Jiang, S.P. Yan, Q.J. Wu, S. Gao and G.L. Wang, *Inorg. Chem. Commun.* **3**, 151 (2000).
[12] H.Z. Kou, S.F. Si, S. Gao, D.Z. Liao, Z.H. Jiang, S.P. Yan, Y.G. Fan and G.L. Wang, *Eur. J. Inorg. Chem.* **2002**, 699 (2002).
[13] T. Miyoshi, T. Iwamoto and Y. Sasaki, *Inorg. Chim. Acta* **7**, 97 (1973).
[14] C. Janiak, H.P. Wu, P. Klüfers and P. Mayer, *Acta Cryst. C* **55**, 1966 (1999).
[15] G.M. Sheldrick, SHELXS-97 and SHELXL-97, Software for Crystal Structure Analysis (Siemens Analytical X-ray Instruments Inc, Madison, WI, 1997).
[16] G. Alzuet, S. Ferrer-Llusar, J. Borrás and R. Martínez-Máñez, *Polyhedron* **19**, 725 (2000).
[17] M.J. Begley, P. Hubberstey and J. Stroud, *Polyhedron* **16**, 805 (1997).
[18] M.R. Ullah, P.K. Bhattacharya and K. Venkatasubramanian, *Polyhedron* **15**, 4025 (1996).
[19] S. Siddiqui and R.E. Shepherd, *Inorg. Chem.* **25**, 3869 (1986).
[20] J. Černák, J. Paharová, J. Skoršepa and W. Massa, *Z. Anorg. Allg. Chem.* **628**, 344 (2002).
[21] C.A. Johns and K.M. Abdul Malik, *Polyhedron* **21**, 395 (2002).
[22] P. Amudha, M. Kandaswamy, L. Govindaswamy and D. Velmurugan, *Inorg. Chem.* **37**, 4486 (1998).
[23] R. Bhalla, M. Helliwell and C.D. Garner, *Inorg. Chem.* **36**, 2944 (1997).