

Square Planar Complexes of Cu(II) with an N₂O Donor Set of a New Schiff Base Ligand: Synthesis and Structural Aspects

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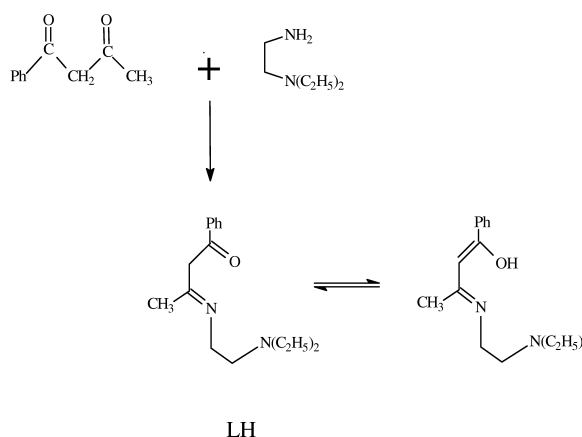
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The title compounds, [Cu(C₁₆H₂₃N₂O)SCN] (**1**) and [Cu(C₁₆H₂₃N₂O)N₃] (**2**), containing a tridentate Schiff base ligand, which is the 1:1 condensation product of benzoylacetone and 2-diethylaminoethylamine, have been synthesised and their crystal structures determined. The structure of **1** is based on a four coordinate copper centre with square-planar geometry formed by the N₂O donor set of the Schiff base and an N atom of the thiocyanate anion. A similar arrangement occurs in **2** with the N₂O donor set of the Schiff base and an N atom of the azide anion. The Cu-N and Cu-O distances are 1.924(8), 2.073(8), 1.927(9) and 1.910(6) Å, for **1** and 1.960(4), 2.050(4), 1.935(4) and 1.907(3) for **2**, respectively.

Key words: Cu(II) Acetate, Crystal Structure, Spectral and Cyclovoltammetric Studies

Introduction

It has been shown that Cu(II) complexes are more active as anti-inflammatory drugs than their parent ligands [1]. Schiff base complexes with various metal ions are of considerable interest with a diverse range of applications in organic synthesis [2, 3]. Such multi-dentate organic ligands [4–6] can accommodate one, two or more metal centers and thus may provide the basis of models for active sites of biological systems [7–9]. In recent years, an increasing effort has been focused on the preparation of mono- or di-nuclear mixed ligand transition metal complexes containing neutral or chelating nitrogen ligands. Early and late transition metal complexes of this type and particularly those of copper have extensively been used as catalysts for a wide variety of reactions, including olefin polymerization [10–12] and oxygen activation [13–15]. The complexity of the stereochemistry of Cu(II) complexes is well known [16–18]. Owing to the plasticity of the coordination sphere, copper(II) ion forms a variety of complexes with coordination number 4–6 [19]. Some square planar copper complexes with an N₂O₂ donor set and with a chelating 2,2'-diamino-4,4'-bi-1,3-thiazole ligand have been recently published [20, 21]. We have reported previously the structure of



Scheme 1.

a monomeric Schiff base complex of copper(II) [22].

In this paper, we report two new mononuclear copper(II) complexes, [Cu(C₁₆H₂₃N₂O)SCN] (**1**) and [Cu(C₁₆H₂₃N₂O)N₃] (**2**), with a new tridentate Schiff base ligand LH (Scheme 1). The complexes have been characterised by elemental analysis, IR and UV-vis spectra, TGA and cyclovoltammetric studies. The structures of the complexes were determined by X-ray diffraction using single crystals.

Table 1. Crystallographic data for **1** and **2**.

	1	2
Empirical formula	C ₁₇ H ₂₃ CuN ₃ OS	C ₁₆ H ₂₃ CuN ₅ O
Formula weight	380.98	364.93
Crystal system	monoclinic	orthorhombic
<i>a</i> (Å)	6.5825(16)	10.6110(18)
<i>b</i> (Å)	13.358(3)	11.6019(16)
<i>c</i> (Å)	19.594(5)	13.684(2)
β (°)	93.79(2)	90
<i>V</i> (Å ³)	1719.0(7)	1684.6(5)
<i>T</i> (K)	100(2)	100(2)
Space group	<i>Cc</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>Z</i>	4	4
Radiation (λ , Å)	0.71073	0.71073
Crystal size (mm ³)	0.04 × 0.62 × 0.10	0.16 × 0.92 × 0.42
θ Range for data collection	3.05 to 24.98°	2.30 to 24.99°
Reflections collected	1647	2248
Independent reflection	1647	2083
	$[R(\text{int}) = 0.0000]$	$[R(\text{int}) = 0.0538]$
Data / restraints / parameters	1647 / 8 / 208	2083 / 0 / 211
Goodness-of-fit on F^2	1.020	1.040
Final R_1/wR_2 indices	0.0526 / 0.1122 ^a	0.0420 / 0.1157 ^a

^a R_1 and wR_2 values are quoted for data with $I > 2\sigma(I)$ and all data, respectively.

Experimental Section

Materials

All chemicals and solvents used were of reagent grade. Benzoylacetone and 2-dimethylaminoethylamine (Fluka), copper acetate, sodium thiocyanate and sodium azide (Loba Chemie, India) were used as received.

Physical techniques

C,H,N analyses were carried out using a Perkin-Elmer 2400 II elemental analyser. The infrared spectra were recorded on a Perkin-Elmer FT-IR instrument in the range of 4000–200 cm^{−1} as KBr pellets. The electronic spectra were measured on a Perkin-Elmer Lambda-40 (UV-VIS) spectrophotometer in dichloromethane. Electrochemical studies were performed on a CH 600A cyclic voltameter instrument using acetonitrile as solvent. Thermal studies were carried out in a Shimadzu TGA-50 thermal analyser under dynamic nitrogen atmosphere at a heating rate of 10 °C min^{−1}.

X-ray crystallography

Green crystals of **1** and **2** were obtained by slow evaporation of methanol solutions, covered in nujol and mounted with vacuum grease on glass fibres on a Bruker AXS P4 diffractometer. Data were collected with Mo-K α radiation (0.71073 Å) at 100 K with an Oxford Cryosystems Cryostream. No significant crystal decay was found. Data were corrected for absorption empirically by means of ψ scans. The structures were solved by direct and difference

Fourier methods and refined by full-matrix least-squares on F^2 . All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic computing was performed using SHELXTL [23] programs. Further details are given in Table 1.

Synthesis of [Cu(C₁₆H₂₃N₂O)SCN] (**1**)

For the preparation of **1**, the ligand (LH), was prepared by refluxing benzoylacetone (0.811 g, 5 mmol) and 2-diethylaminoethylamine (0.711 ml, 5 mmol) in 30 ml of methanol for half an hour. Then the resulting mixture gave a yellow solution containing the tridentate ligand (LH). To 20 ml of a methanolic solution of copper(II) acetate (0.399 g, 2 mmol), the ligand LH (2 mmol) was added followed by the slow addition of 10 ml of a methanolic solution of sodium thiocyanate (0.162 g, 2 mmol). The mixture was kept at room temperature. After a few days green crystals of **1** formed on slow evaporation of the solvent. Crystals suitable for X-ray diffraction were collected. Yield 60%. – Analysis for [Cu(C₁₆H₂₃N₂O)SCN]: calcd. C 53.54, H 6.03, N 11.02, Cu 16.66; found C 53.51, H 5.97, N 11.01, Cu 16.62.

Synthesis of [Cu(C₁₆H₂₃N₂O)N₃] (**2**)

Complex **2** was prepared by the procedure adopted for **1**, using sodium azide instead of sodium thiocyanate. Yield 65%. – Analysis for [Cu(C₁₆H₂₃N₂O)N₃]: calcd. C 52.61, H 6.30, N 19.18, Cu 17.40; found C 52.58, H 6.28, N 19.15, Cu 17.36.

Results and Discussion

IR spectra

A weak broad band in the region 3250–3350 cm^{−1} due to a hydrogen bonded OH group in free Schiff base was not observed in the infrared spectra of **1** and **2**. This indicates that the enolic oxygen atom is deprotonated and coordinated to the Cu(II) center. Several criteria have been considered to ascertain the bonding mode of thiocyanate [24]. The ν (C \equiv N) absorption at \sim 2100 cm^{−1} for **1** suggests the presence of an N-coordinated SCN group. ν_a (NNN) appeared at 2042 cm^{−1} for **2**.

Electronic spectra

Electronic spectra of copper Schiff base complexes can be an indicator of geometry [25, 26]. The electronic spectra of **1** in dichloromethane solution shows an absorption band in the region of 345 for **1** and 352 nm for **2** indicating a four coordinate square planar geometry of Cu(II) [27]. The bands at 246, 222 nm

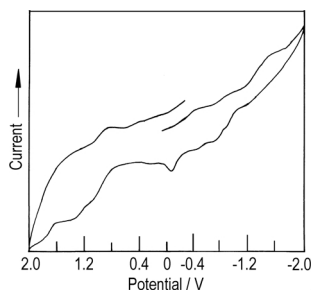


Fig. 1. Cyclic voltammogram of complex **1** (—) in acetonitrile solution using a platinum electrode at a scan rate of 50 mVs⁻¹, with Et₄N.CIO₄ as supporting electrolyte.

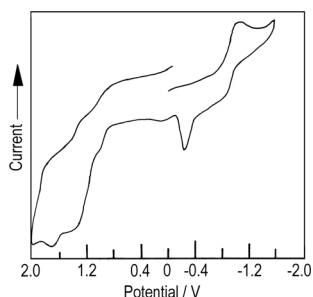


Fig. 2. Cyclic voltammogram of complex **2** (—) in acetonitrile solution using a platinum electrode at a scan rate of 50 mVs⁻¹, with Et₄N.CIO₄ as supporting electrolyte.

for **1** and 248, 214 nm for **2** may be assigned to intra-ligand charge transfer transitions.

Electrochemical study

The electrochemical studies of the complexes were performed using acetonitrile as solvent and tetrabutylammonium perchlorate as supporting electrolyte at a scan rate of 50 mVsec⁻¹. The cyclic voltammetry diagrams of the complexes **1** and **2** show one reductive response each on the negative side of SCE (at -1.59 V, -0.99 V) which are irreversible in nature for the reduction of a Cu(II) center. Two irreversible oxidation responses are also observed at (+1.04 V, +1.03 V) and (+1.45 V, +1.74 V) for complex **1** and **2**, respectively, which are due to the oxidation of coordinated ligands. The results suggest that the Cu(I) species are unstable and undergo rapid decomposition. The cyclic voltammograms of **1** and **2** are shown in Fig. 1 and Fig. 2, respectively.

Thermal analysis

The thermal decomposition trace of complex **1** has been recorded. A thermal study of complex **2** was not

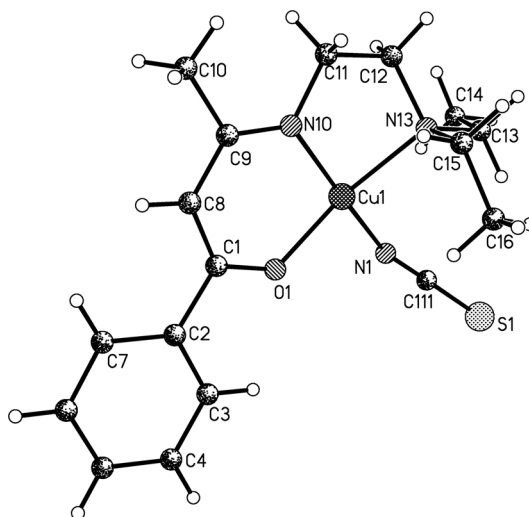


Fig. 3. Perspective view of complex **1** with atom numbering scheme.

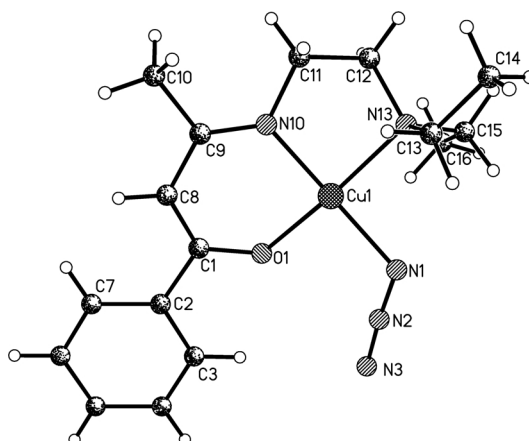


Fig. 4. Perspective view of complex **2** with atom numbering scheme.

carried out in order to avoid explosion of the azide. Complex **1** is stable up to ~ 190 °C. Then it undergoes decomposition. The mass loss in the temperature range 190–320 °C is consistent with the loss of one molecule of the Schiff base moiety.

Crystal structure

The molecular structures of **1** and **2** along with the atom numbering schemes are shown in Fig. 3 and Fig. 4, respectively. The complexes feature a four coordinate copper center with the NNO donor set of the Schiff base and an N atom of the thiocyanate ion (**1**) or the azide ion (**2**). The square plane in each case suf-

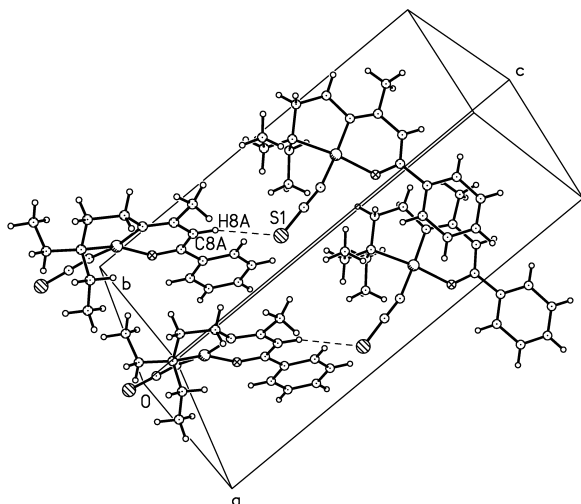


Fig. 5. Crystallographic packing diagram of **1** including hydrogen bonding.

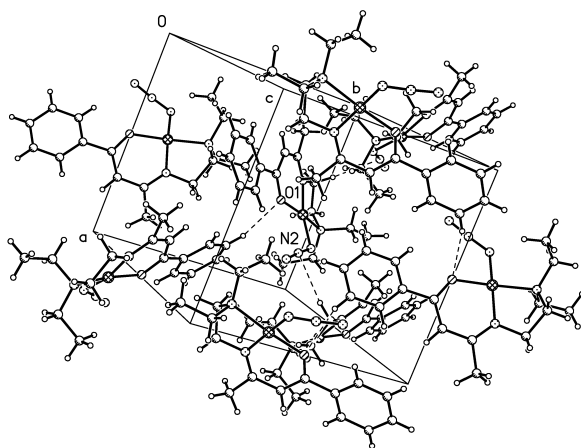


Fig. 6. Crystallographic packing diagram of **2** including hydrogen bonding.

fers a small tetrahedral distortion as indicated by the deviations of the relevant atoms from the mean plane of the N₃O atoms (Table 4). The distortions are quite significant and this probably reflects the greater steric demand of the ethyl substituents on N(13). Angular distortions in the square plane are also caused by the different bite angles in the five- and six-membered chelate rings. The distortion of the structures from square planar to tetrahedral can be evaluated through the parameter Δ introduced by Galy *et al.* [28] and applied by Ribas and Kahn [29].

Thus the angles N(10)-Cu(1)-N(13) (84.2(3) for **1**, 85.66(15)° for **2**, O(1)-Cu(1)-N(1) (89.7(3)° for **1** and O(1)-Cu(1)-N(10) (92.68(14)° for **2** are respectively

Table 2. Selected bond lengths [Å] and angles [°] for **1**.

Cu(1)-O(1)	1.910(6)	Cu(1)-N(10)	1.924(8)
Cu(1)-N(1)	1.927(9)	Cu(1)-N(13)	2.073(8)
C(9)-N(10)	1.305(14)	C(4)-C(5)	1.363(14)
C(5)-C(6)	1.377(14)		
O(1)-Cu(1)-N(10)	94.1(3)	O(1)-Cu(1)-N(1)	89.7(3)
N(10)-Cu(1)-N(1)	170.9(4)	O(1)-Cu(1)-N(13)	161.7(3)
N(10)-Cu(1)-N(13)	84.2(3)	N(1)-Cu(1)-N(13)	94.8(3)
N(1)-C(11)-S(1)	178.6(9)	C(11)-N(1)-Cu(1)	160.7(9)

Table 3. Selected bond lengths [Å] and angles [°] for **2**.

Cu(1)-O(1)	1.907(3)	Cu(1)-N(1)	1.960(4)
Cu(1)-N(10)	1.935(4)	Cu(1)-N(13)	2.050(4)
N(1)-N(2)	1.205(6)	N(2)-N(3)	1.161(6)
C(9)-N(10)	1.302(6)	C(4)-C(5)	1.394(7)
C(5)-C(6)	1.389(7)		
O(1)-Cu(1)-N(10)	92.68(14)	O(1)-Cu(1)-N(13)	172.12(15)
O(1)-Cu(1)-N(1)	90.83(15)	N(10)-Cu(1)-N(13)	85.66(15)
N(10)-Cu(1)-N(1)	168.26(17)	N(1)-Cu(1)-N(13)	92.32(16)
N(3)-N(2)-N(1)	176.0(5)	N(2)-N(1)-Cu(1)	118.9(3)

Table 4. Deviations of atoms (Å) from the least-squares plane through O(1), N(1), N(10), N(13).

Atoms	1	2
O(1)	0.2343 (0.0044)	0.1633 (0.0019)
N(1)	-0.2225 (0.0042)	-0.1566 (0.0018)
N(10)	-0.2366 (0.0044)	-0.1662 (0.0019)
N(13)	0.2248 (0.0042)	0.1595 (0.0018)

Rms deviations of fitted atoms O1, N1, N10, N13 are 0.2296 for **1** and 0.1614 for **2**.

Table 5. Hydrogen bonds for **1** and **2** [Å and °].

Comp.	D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
1	C(8)-H(8A)...S(1) ^{#1}	0.95	2.93	3.824(10)	156.6
2	C(11)-H(11A)...N(2) ^{#1}	0.99	2.57	3.536(6)	165.1
2	C(6)-H(6)...O(1) ^{#2}	0.95	2.51	3.422(5)	161.2

Symmetry transformations used to generate equivalent atoms: ^{#1} $x + 1/2, -y + 1/2, z + 1/2$ for **1**; ^{#1} $x - 1/2, -y + 3/2, -z + 1$ and ^{#2} $x - 1/2, -y + 5/2, -z + 1$ for **2**.

less and greater than the ideal value of 90°. The *trans* angles N(10)-Cu(1)-N(1) and O(1)-Cu(1)-N(13) are 170.9(4)° for **1**, 168.26(17)° for **2** and 161.7(3)° for **1**, 172.12(15)° for **2** respectively which deviates from the ideal bond angle 180°. The Cu-N distances to the amino nitrogen atom N(13) (2.073(8) for **1**, 2.050(4) for **2** Å) are longer than the corresponding values involving the imino nitrogen atom N(10) (1.924(8) for **1**, 1.935(4) for **2** Å). The Cu-N distances in **1** and **2** are quite different from other reported Cu-N distances in the range 1.990(2)–2.004(6) Å, as in DABT [2,2'-diamino-4,4'-bi-1,3-thiazole] [21] and 2,2'-bipyridine complexes of Cu^{II} [30,31]. The Cu-O bond lengths (1.910(6) for **1**, 1.907(3) Å for **2**) are comparable with those found in other Cu(II) complexes. The

N(10)–C(11)–C(12)–N(13) bridge is puckered in both the complexes with dihedral angles $-34.6(10)$ for **1**, $-46.0(5)^\circ$ for **2**.

The NCS group in **1** is almost linear but the coordination to the metal ion has a considerable deviation from linearity (N(1)–C(111)–S(1)/Cu(1)–N(1)–C(111) = $178.6(9)/160.7(9)^\circ$). The NNN group in **2** is nearly linear and shows a bent coordination mode with the metal (N(1)–N(2)–N(3)/Cu(1)–N(1)–N(2) = $176.0(5)/118.9(3)^\circ$). The NNN moiety is bent away from the dialkylamine and inclined towards the benzophenone moiety. The N(1)–N(2) bond ($1.205(6)$ Å in the complex **2**) is longer than the N(2)–N(3) bond ($1.161(6)$ Å) suggesting a higher contribution of the first canonical form: $\text{Cu}-\text{N}=\text{N}=\text{N} \leftrightarrow \text{Cu}-\text{N}=\text{N}=\text{N}$. The six membered ring defined by the metal and the benzoylacetone is almost planar in **1**, and slightly puckered in **2**. A close scrutiny of the bond lengths in the ligands reveals that in both complexes the N(10)–C(9) bond retains its double bond character and within the phenyl ring (Table 2 and Table 3).

In case of complex **1** a weak hydrogen bond contact is present between H8 and S1 of the neighbouring molecule (Table 5). For **2**, two varieties of hydrogen bonds are shown in the packing diagram (Fig. 6). The

H...O/N distances lie in the range $1.767-2.519$ Å and fall within the acceptable limits of hydrogen bond interactions [32]. The N(2) azide nitrogen atom acts as an H acceptor generating a hydrogen bond with H(11A) of bond length 2.57 Å. Another C–H...O type intermolecular hydrogen bond is present in **2**, with H(6)–C(6) acting as the hydrogen-bond donor and O(1) as the acceptor (Table 5). These two types of hydrogen bond interactions are responsible for the two dimensional character of the structure **2** (Fig. 6).

Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC reference numbers 223967 and 223968 for **1** and **2**, respectively. Copies of the information may be obtained free of charge from The Director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www.http://www.ccdc.cam.ac.uk).

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- [1] J. R. J. Sorenson, *Prog. Med. Chem.* **26**, 437 (1989) and refs. therein.
- [2] T. Katsuki, *Coord. Chem. Rev.* **140**, 189 (1995).
- [3] Y. N. Ito, T. Katsuki, *Bull. Chem. Soc. Jpn.* **72**, 603 (1999).
- [4] D. Garnovshii, A. L. Nivorozhkin, V. I. Minkin, *Coord. Chem. Rev.* **126**, 1 (1993).
- [5] K. Wieghardt, I. Tolkdrof, W. Herrmann, *Inorg. Chem.* **24**, 1230 (1985).
- [6] D. H. Lee, N. N. Murthy, K. D. Karlin, *Inorg. Chem.* **35**, 804 (1996).
- [7] Copper Coordination Chemistry, in K. D. Karlin, J. Zubieta (eds): *Biological and Inorganic Perspectives*, p. 1–22, Adenine Press, New York (1983).
- [8] N. Kitajima, Y. Muraoka, *Chem. Rev.* **94**, 737 (1994).
- [9] E. I. Solomon, M. J. Baldwin, M. D. Lowery, *Chem. Rev.* **106**, 25 (1990).
- [10] C. M. Killian, D. J. Tempel, L. K. Johnson, M. Brookhart, *J. Am. Chem. Soc.* **118**, 11664 (1996).
- [11] L. K. Johnson, C. M. Killian, M. Brookhart, *J. Am. Chem. Soc.* **117**, 6414 (1995).
- [12] G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem. Int. Ed.* **38**, 428 (1999).
- [13] B. Jung, K. D. Karlin, A. D. Zuberbuhler, *J. Am. Chem. Soc.* **118**, 3763 (1996).
- [14] P. L. Holland, K. R. Rodgers, W. B. Tolman, *Angew. Chem. Int. Ed.* **38**, 1139 (1999).
- [15] S. J. Lange, H. Miyake, L. Que (Jr.), *J. Am. Chem. Soc.* **121**, 6330 (1999).
- [16] B. P. Murphy, *Coord. Chem. Rev.* **124**, 63 (1993).
- [17] B. J. Hathaway, *Struct. Bonding (Berlin)* **57**, 55 (1984).
- [18] J. Gajo, R. Boca, E. Jona, M. Kabesova, L. Macaskova, J. Sima, *Coord. Chem. Rev.* **43**, 87 (1982).
- [19] B. J. Hathaway, *Comprehensive Coordination Chemistry*, Vol. 5, p. 606, Pergamon, Oxford (1987).
- [20] M. Kabak, A. Elmali, Kavlakoglu, Y. Elerman, Y. E. Durlu, *Acta Crystallogr.* **C55**, 1650 (1999).
- [21] J.-G. Liu, J.-J. Nie, D.-J. Xu, Y.-Z. Xu, J.-Y. Wu, M. Y. Chiang, *Acta Crystallogr.* **C57**, 354 (2001).
- [22] A. Datta, N. K. Karan, S. Mitra, G. M. Rosair, Z. Naturforsch. **57b**, 999 (2002).
- [23] G. M. Sheldrick, SHELXTL. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA (1999).
- [24] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 3rd ed., Wiley, New York (1978).
- [25] N. M. Atherton, D. E. Fenton, G. J. Hewson, C. H. McLean, *J. Chem. Soc., Dalton Trans.* 1059 (1988).
- [26] B. J. Hathaway, R. J. Dudley, P. Nicholls, *J. Chem. Soc. A*, 1845 (1969).

- [27] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, 2nd ed., Elsevier, Amsterdam (1984).
- [28] J. Galy, J. J. Bonner, S. Anderson, *Acta Chem. Scand.* **A33**, 383 (1979).
- [29] J. Ribas, C. Diaz, R. Costa, Y. Journaux, C. Mathoniere, O. Kahn, A. Gleizes, *Inorg. Chem.* **29**, 2042 (1990).
- [30] D. Xu, A. Xie, Y. Xu, C. Zhang, W. Chen, *J. Coord. Chem.* **39**, 273 (1996).
- [31] L. Zhang, D. Xu, Y. Xu, J. Gu, *Acta Crystallogr.* **C53**, 299 (1997).
- [32] K. Takuhashi, Y. Nishida, K. Kida, *Bull. Chem. Soc. Jpn.* **57**, 2628 (1984).