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Anna Mašlejová^a; Ivan Potočák^a; Jozef Šima^a; Mária Kabešová^a

^a Department of Inorganic Chemistry, Slovak Technical University, Bratislava, Slovakia

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PHYSICAL PROPERTIES AND STRUCTURES OF PSEUDOHALOGENOCOPPER(II) COMPLEXES WITH PHENANTHROLINE

ANNA MAŠLEJOVÁ^a,* IVAN POTOČNÁK^a, JOZEF ŠIMA^a, and MÁRIA
KABEŠOVÁ^a,

^a*Department of Inorganic Chemistry, Slovak Technical University, 812 37 Bratislava,
Slovakia*

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Electronic, IR and EPR spectra of eight Cu(II) complexes with trigonal-bipyramidal, tetragonal-bipyramidal and tetragonal-pyramidal coordination polyhedra containing phenanthroline and pseudohalogenide ligands were examined and their interrelationships with molecular and crystal structures evaluated. Along with the usual trigonal-bipyramidal environment of Cu(II), tetragonal symmetry for four complexes was observed. The origin of this tetragonal symmetry is connected with intermolecular interaction of phenanthroline with pseudohalide ligands.

Keywords: copper(II); phenanthroline; pseudohalide; structure; spectroscopy

INTRODUCTION

The known molecular and crystal structures of copper(II) complexes of 1,10-phenanthroline (phen) can be grouped into two classes on the basis of coordination number. Complexes belonging to the first class have coordination number five. The trigonal-bipyramidal arrangement around Cu(II) is observed if the *bis*(phenanthroline)copper(II) complex fragment contains monodentate anionic ligands such as chloro [1], iodo [2], cyano [3] groups. The tetragonal pyramid is observed if the *bis*(phenanthroline)copper(II) fragment contains monodentate, neutral, bulky ligands such as 3,5-dimethylpyridine [4]. If the fifth coordination site is occupied by water, distortion of the coordination polyhedron between the trigonal-bipyramid [5] and the tetragonal pyramid [6] is observed.

* Author for correspondence.

Complexes having coordination number six fall into the second class. The coordination number six is reached in three ways. If the complex contains bidentate ligands such as acetato [7] or nitrito [8] anions, mostly the 4 + 1 + 1* arrangement related to *cis*-distorted octahedral stereochemistry occurs. *Cis*-arrangement of ligands in the equatorial plane also was observed in the structures of [Cu(phen)₂X₂] compounds (X = NCS, NCSe) [9]. Two monodentate pseudohalide ligands in the coordination sphere with *cis*-arrangement were also observed in the structure of the compound with X = N(CN)₂, one ligand X occupies, however, an axial position [10]. In both previous cases distorted tetragonal-bipyramidal structures are formed.

We have carried out spectroscopic and crystallo-chemical investigations of eight Cu(II) complexes of 1,10-phenanthroline with known molecular and crystal structures, [Cu(phen)₂CN]NO₃·H₂O (I) [3], [Cu(phen)₂CN]C(CN)₃·2H₂O (II) [11], [Cu(phen)₂NCS]C(CN)₃ (III) [12], [Cu(phen)₂NCS]ONC(CN)₂ (IV) [13], [Cu(phen)₂(NCS)₂] (V) [9], [Cu(phen)₂(NCSe)₂] (VI) [9], [Cu(phen)₂{N(CN)₂}]₂ (VII) [10] and [Cu(phen)(NCO)₂]₂ (VIII) [14]. Our attention was directed toward the coordination geometry of the central atom, the character of copper(II)—ligand bonds and the electronic structure of the central ion. As interligand steric repulsion often causes distortion of the configuration around the central atom, we have also paid attention to intermolecular interactions in the complexes. The non-covalent interligand interactions, which make significant contributions to the stereochemistry and other features of copper(II) complexes, are discussed.

EXPERIMENTAL

Preparations

Compound (I) was prepared according to a published procedure [3]; the other complexes were available from previous work [9-14].

Physical Measurements

IR spectra (4000-200 cm⁻¹) were recorded using a Philips Analytical PU 9800 FTIR spectrophotometer in nujol or CsI. Electronic spectra in the region 12500-30000 cm⁻¹ were measured on a Specord UV-VIS spectrophotometer also in nujol. Electronic absorption spectra in the range 50000-25000 cm⁻¹ were recorded on Specord M-40 equipment, suspensions of samples in carbohydrates *n*-C₁₇H₃₆ or *n*-C₈H₁₈ having been placed between two parallel quartz windows. ESR spectra at room temperature were recorded on a Bruker SRC 200D spectrometer operating at X-band frequencies.

RESULTS AND DISCUSSION

IR Spectra

The CN stretch increases to 2137 cm^{-1} for complex (I) compared with 2080 cm^{-1} for ionic, noncoordinated cyanide in KCN, showing a copper—cyanide interaction. The split in the ν_3 band of nitrate ion (reaching 59 cm^{-1}) does not indicate semicoordination between the copper(II) atom and the nitrate [3], but suggests the presence of a hydrogen bond between a water hydrogen atom and a nitrate oxygen atom. The free tricyanomethanide anion is characterised by a sharp, high-intensity CN stretch at 2176 cm^{-1} in the potassium salt. The very strong band at 2168 cm^{-1} for complex (II) is then assigned to $\nu(\text{C}\equiv\text{N})$ of $\text{C}(\text{CN})_3^-$ and the shoulder to $\nu(\text{CN})$ from a cyanide group. The medium bands at 1223 and 1260 cm^{-1} are assigned to $\nu(\text{C}-\text{C})$ and the strong band at 559 cm^{-1} to $\nu(\text{C}-\text{C}\equiv\text{N})$ of the $\text{C}(\text{CN})_3^-$ ion [15]. Broad and rather complex bands involving $\nu(\text{OH})$ stretches in (I) and (II) are concentrated at approximately 3400 cm^{-1} and are characteristic of water molecules bonded by hydrogen bridges [16]. In complex (III) the band at 2159 cm^{-1} is assigned to $\nu(\text{C}\equiv\text{N})$ of the $\text{C}(\text{CN})_3^-$ ion and the band at 2085 cm^{-1} to $\nu(\text{CN})$ of the NCS group. The position of $\nu(\text{CN})$, $\nu(\text{CX})$ and $\delta(\text{NCX})$ for complexes (III), (IV), (V) and (VI) falls in the range observed for NCX groups end-bonded by nitrogen atoms. Very sharp bands near $\nu(\text{CN})$ band were observed for (V) and (VI), probably ^{13}C satellites as predicted by first-order calculation [17]. The absorption bands corresponding to $\nu_{\text{as}}(\text{C}-\text{N}=\text{O})$ at 1310 and 1343 cm^{-1} , $\nu_{\text{s}}(\text{C}-\text{N}=\text{O})$ at 1248 and 1258 cm^{-1} and $\delta(\text{N}=\text{O})$ at 799 cm^{-1} were observed in the IR spectrum of (IV). Some of the vibrations of the nitrosodicyanomethanide ion are slightly shifted compared with the free ion [18]. This shift may be due to different measurement technique. The $\nu(\text{C}\equiv\text{N})$ frequency values are usually used as a criterion for the bonding mode of the dicyanamide ligand [15]. The band at 2296 cm^{-1} observed in the IR spectrum of (VII) can be assigned to $\nu_{\text{s}} + \nu_{\text{as}}(\text{C}-\text{N})$. The shift of $\nu_{\text{s}}(\text{C}\equiv\text{N})$ towards lower wavenumbers suggests monodentate function of the dicyanamide ligand [19], as confirmed by X-ray analysis of (VII). X-ray analysis of (VIII) shows [14] that the crystal structure consists of dimeric units held together by van der Waals forces. The surrounding of each Cu(II) atom is distorted square planar with average Cu-N(NCO) and Cu-N(phen) distances of $1.905(10)\text{ \AA}$ and $2.010(10)\text{ \AA}$, respectively. Our thorough study has confirmed that dimers are stacked, forming Cu-Cu chains. The Cu...Cu distances are 4.0 \AA and 3.2 \AA between dimers and within each dimer, respectively. Moreover, we have found an asymmetrically bridging, bonded nitrogen atom of the NCO group with the longer distance Cu-N(NCO) of $2.449(10)\text{ \AA}$. Consequently, the coordination polyhedron is a distorted tetragonal

pyramid. NCO bridging *via* the nitrogen atom causes [20] great splitting of the $\delta(\text{NCO})$ mode by $\approx 30\text{--}90\text{ cm}^{-1}$. In (VIII) the $\delta(\text{NCO})$ split cannot be estimated since a phen band occurs in the pertinent region. The split of the $\nu(\text{CN})$ band in (VIII) indicates lower symmetry for the studied complex [20].

In the far-infrared region there occur two to four absorption which can be attributed to Cu-N stretching vibrations. An approximate assignment of some of the observed bands can be made. Those in the region $252\text{--}241\text{ cm}^{-1}$ can be assigned to the Cu-N(phen) stretch, while those in the range $363\text{--}280\text{ cm}^{-1}$ can be attributed to Cu-N(anion).

ESR Spectra

Complex (I) exhibits a reversed orthorhombic ESR spectrum (Table I) with unresolved hyperfine splitting at g_{\parallel} . Such a spectrum can be observed for Cu(II) in a distorted trigonal-bipyramidal stereochemistry. The ESR spectrum of (II) is an orthorhombic one, but the value $R = (g_2 - g_1)/(g_3 - g_2) = 1.425$ may reveal d_{z^2} ground state [21]. Compounds (III) and (IV) furnish axial spectra, which are reversed in form $g_{\perp} \gg g_{\parallel} > 2.0$ and consistent with the d_{z^2} ground state. Compound (V) exhibits a normal orthorhombic ESR spectrum. The $(g_2 - g_1)/(g_3 - g_2)$ ratio is 0.57, clearly indicating the $d_{x^2 - y^2}$ ground state. However, the low G value (2.86) indicates that molecular axes of the basic units are misaligned to some extent and, consequently, the crystal g-values deviate from the g-factors of the molecular configuration.

ESR spectra of (VI), (VII) and (VIII) show normal axial features; only (VI) has no recognisable g_{\parallel} value. The signal at g_{\parallel} in (VII) is very broad and can be connected with the presence of unresolved hyperfine splitting. Therefore the estimated value $g_{\parallel} = 2.478$ is not reliable. The G value over 5.0 suggests the presence of exchange coupling in these complexes due to misalignment of the coordinate axes of the different copper(II) atoms present in the unit cell.

Electronic Spectra

The solid state LF electronic spectra of (I)-(VII) (Table II) generally consist of a broad high frequency band ($12250\text{--}14400\text{ cm}^{-1}$), occasionally with a low frequency shoulder ($11200\text{--}12100\text{ cm}^{-1}$) only partially resolved. The maxima of the d-d transitions lie in the region predicted for tetragonal-bipyramidal or trigonal-bipyramidal stereochemistry [20]. The absorption band at 20700 cm^{-1} observed in (IV) is associated to an intraligand absorption in $\text{ONC}(\text{CN})_2^-$ and the shoulder at 24500 cm^{-1} probably contains a contribution of ligand-to-metal CT and/or intraligand absorption.

TABLE I IR data for the copper(II) complexes with 1,10-phenanthroline [cm^{-1}].^a

Compound	$\nu(\text{CN})$	$\nu(\text{CX})$	$\delta(\text{NCX})$	$\nu(\text{Cu-N})$
[Cu(phen) ₂ CN]NO ₃ ·H ₂ O	I 2137 w, br			359 w, 247 m
[Cu(phen) ₂ CN]C(CN) ₃ ·2H ₂ O	II 2168 vs, 2157 vs			361 m, 299 m, 248 m
[Cu(phen) ₂ NCS]C(CN) ₃	III 2159 vs ^b , 2085 vs ^b			299 m, 272 m, 237 m
[Cu(phen) ₂ NCS]ONC(CN) ₂	IV 2207 vs ^b , 2193 vs ^b , 2089 vs	849 m	475 m	355 m, 249 m, 243 m
[Cu(phen) ₂ (NCS) ₂]	V 2120 vs, 2093 vs	847 m	471 m	318 m, 287 m, 248 m, 241 m
[Cu(phen) ₂ (NCSe) ₂]	VI 2105 vs, 2054 vs	845 m	475 m	299 m, 280 m, 243 m
[Cu(phen) ₂ {N(CN) ₂ }] ₂	VII 2296 vs ^b , 2240 vs, 2199 m, 2174 vs, 2135 vs	644 m	422 m	310 m, 287 m, 247 m
[Cu(phen)(NCO) ₂] ₂	VIII 2226 vs, 2180 vs	1341 m	608 m, 617 m, 648 m ^c	363 m, 262 m, 252 m

^aS-strong, m - medium, w - weak, v - very, br - broad. See text. Cannot be distinguished from the phen ligand band.

TABLE II Electronic and ESR spectroscopic data for the copper(II) complexes with 1,10-phenanthroline.

Compound	ν_{max} [10^{-3} cm^{-1}]	g_{\perp} or g_1	g_2	g_{\parallel} or g_3
[Cu(phen) ₂ CN]NO ₃ ·H ₂ O	I 13.5	36.1	2.180	2.103
[Cu(phen) ₂ CN]C(CN) ₃ ·2H ₂ O	II 13.1	33.5 sh, 36.3	2.011	2.125
[Cu(phen) ₂ NCS]C(CN) ₃	III 12.05	24.0sh ^a , 32.8 sh	42.0	2.229
[Cu(phen) ₂ NCS]ONC(CN) ₂	IV 11.2 sh	20.7, 24.5sh ^a , 33.0 sh, 36.0	33.0 sh, 36.0	43.8
[Cu(phen) ₂ (NCS) ₂]	V 12.1 sh	13.25, 26.0sh, 32.3 sh,	35.5	2.053
[Cu(phen) ₂ (NCSe) ₂]	VI 12.1 sh	23.4sh, 36.1	41.5	2.127
[Cu(phen) ₂ {N(CN) ₂ }] ₂	VII 14.4	31.0sh, 36.0	2.061	2.478
[Cu(phen)(NCO) ₂] ₂	VIII 15.9	31.0sh, 33.1 sh,	42.0	2.039
				2.266

^aThe band contains a contribution of CT and/or intraligand absorption.

TABLE III Interatomic distances [\AA] in the copper(II) complexes with 1,10-phenanthroline.

Compound		$C(\text{phen})-C(\text{phen})$	$C(\text{phen})-X^{\text{a}}$	$C(\text{phen})-Y^{\text{b}}$
$[\text{Cu}(\text{phen})_2\text{CN}]\text{NO}_3 \cdot \text{H}_2\text{O}$	I	3.441	3.483	3.112
$[\text{Cu}(\text{phen})_2\text{CN}]\text{C}(\text{CN})_3 \cdot 2\text{H}_2\text{O}$	II	3.495	3.582	3.211
$[\text{Cu}(\text{phen})_2\text{NCS}]\text{C}(\text{CN})_3$	III	3.407	3.624	3.191
$[\text{Cu}(\text{phen})_2\text{NCS}]\text{ONC}(\text{CN})_2$	IV	3.411	3.552	3.173 (N) 3.063(O)
$[\text{Cu}(\text{phen})_2(\text{NCS})_2]$	V	3.493	3.349	
$[\text{Cu}(\text{phen})_2(\text{NCSe})_2]$	VI	3.570	3.233	
$[\text{Cu}(\text{phen})_2\{\text{N}(\text{CN})_2\}_2]$	VII	3.469	3.238 N(cyano)	3.224 N(amido)
$[\text{Cu}(\text{phen})(\text{NCO})_2]_2$	VIII	3.345	3.126 (linear)	3.304 (bent)

^aX is coordinated anion. ^bY is out-of-sphere anion.

The electronic absorption spectrum of (VIII) exhibits a broad band with a maximum at about 15900 cm^{-1} . Such a spectrum is characteristic for Cu(II) complexes of pronounced tetragonal structure which can be tetragonal-octahedral, rhombic-octahedral or square-based pyramidal. X-ray analysis confirms the latter.

In the UV region, (V)-(VIII) exhibit another shoulder (Table II) which can be assigned to a charge-transfer transition band [22] connected with electron

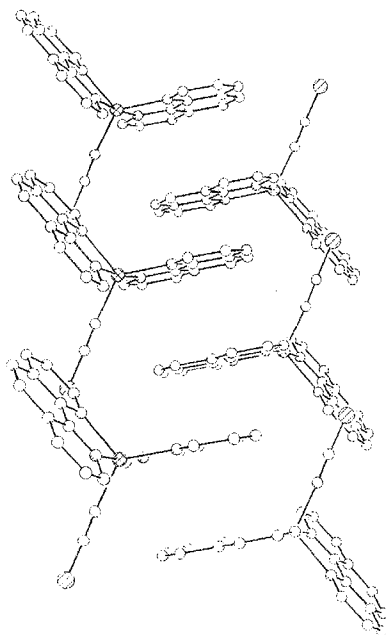


FIGURE 1 Intermolecular interaction in the five-coordinate compounds between parallel phenanthroline molecules. Out-of-sphere anions are omitted for the sake of clarity.

transfer from σ -molecular orbitals of NCS groups to $d_{x^2 - y^2}$ orbitals of the Cu(II) atom. The absorption spectrum of 1,10-phenanthroline in the UV region consists of two structured peaks. The more intense is centred at 43100 cm^{-1} , the less intense one at 37900 cm^{-1} . Shoulders are present at 44000 , 38900 , 36500 , 35000 and 34400 cm^{-1} . The position of the peak maximum of a phenanthroline-localised intraligand transition centred at 43100 cm^{-1} in the free ligand is shifted to higher energy in (I), (II) and (IV) and to lower energy side in the remaining complexes. The absorption band centred at 37900 cm^{-1} , linked to another intraligand transition, is shifted in the spectra of all investigated complexes to lower energy.

Crystal Structures and Weak Interactions

Intermolecular interactions between phenanthroline ligands of neighbouring units have been found in all studied complexes. The shortest distances between carbon atoms of the closest phen molecules coordinated to neighbouring Cu(II) atoms are listed in Table III.

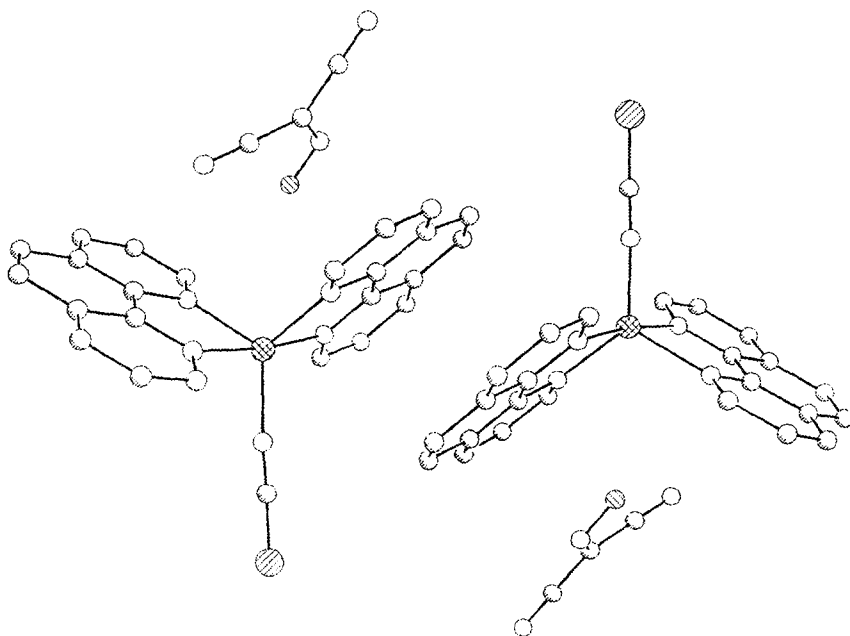


FIGURE 2 Intermolecular interactions between uncoordinated dicyanonitrosomethanide anions and phenanthroline molecules in (IV).

In addition, in the five-coordinate complexes (I)-(IV), supplementary contacts between the oxygen and nitrogen atoms of the counter anions and phenanthroline carbon atoms were found (Table III). Weak interactions in complexes between phenanthroline molecules of neighbouring units and between phenanthroline molecules and counter anions as well as shown in Figures 1 and 2, respectively.

Moreover, in (V)-(VIII) with tetragonal configuration of Cu(II), some additional interactions of monodentate coordinated pseudohalide ligands with the π -system of phenanthroline molecules have been observed (Table III). The most peculiar structural features of (V) and (VI) are short intermolecular distances between the terminal sulphur (selenium) atom of the thiocyanate (selenocyanate) ligands of one complex and phenanthroline molecules of its closest neighbour (Figure 3). The stacking in (VII) differs in some extent. While the thiocyanate and selenocyanate ligands in (V) and (VI) occupy equatorial *cis*-positions, one dicyanamide anion in (VII) occupies an axial and the second an equatorial position. This difference can affect the weak interactions (Figure 4) involving phen molecules and both nitrogen (cyano and amido) atoms of the dicyanamide ligands in the crystal structure. The same arrangement of ligands in

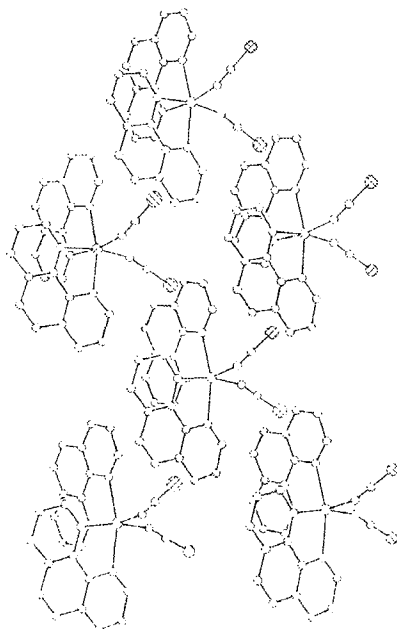


FIGURE 3 Intermolecular contacts between coordinated NCS (NCS_e) groups and phenanthroline molecules in (V) ((VI)).

the coordination polyhedron was observed in the structures of $[\text{Cu}(\text{phen})_2\text{Cl}(\text{NCS})]$ [23] and $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})(\text{ONC}(\text{CN})_2)]\text{ONC}(\text{CN})_2$ [24].

Stacking in complex (VIII) is shown in Figure 5. Interaction of the oxygen atom of coordinated cyanate ligand with phenanthroline is such that the linear cyanate group in the equatorial plane is oriented between two parallel π -systems of phenanthroline molecules of neighbouring molecules. If such an $\text{Cu-NCO}\dots\text{phen-Cu}$ interaction really exists it would affect the electronic properties of the phen ligands, which, consequently, should be observable in their intraligand absorption spectra. Data in Table II suggest this to be the case. The nitrogen atom of the other cyanate group is bonded to two $\text{Cu}(\text{II})$ atoms forming dimers. This causes bending of the cyanate group from the equatorial plane and its orientation between two coplanar phen molecules.

All distances between atoms involving weak interactions are shorter than the sum of the van der Waals radii of the corresponding atoms. Similar contacts have been found between iodine atoms and 2,2'-bipyridine (bpy) in the crystal structure of $\text{Cu}(\text{bpy})(4\text{-iodophenylalanine})$ [25].

We assume the abovementioned interactions are between electrons of oxygen, nitrogen, sulphur and selenium atoms and empty, antibonding π orbitals of

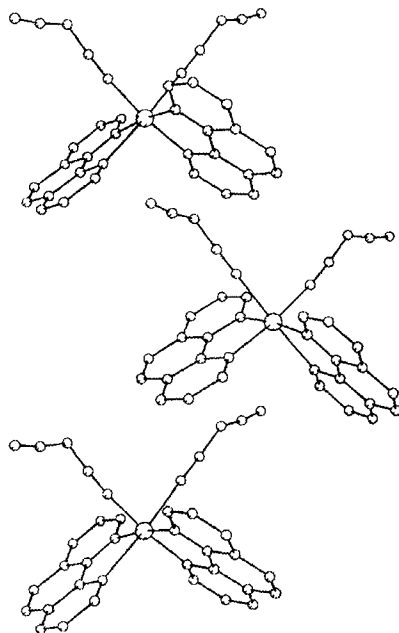


FIGURE 4 Intermolecular contacts between coordinated $\text{N}(\text{CN})_2$ anions and phenanthroline molecules in (VII).

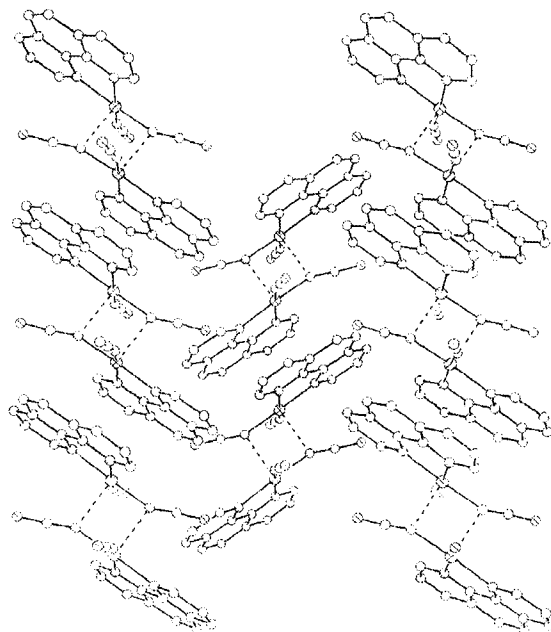


FIGURE 5 NCO anions and their intermolecular interactions with phenanthroline molecules in (VIII).

phenanthroline molecules. Such intermolecular interactions can cause a change in the ligand field strength of the phenanthroline ligands; this manifests in changes of energy level splitting and also in the different form of the coordination polyhedron.

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