

Metal complexes of pyrroline-N-oxide dioxime

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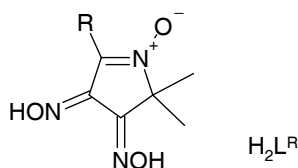
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Syntheses and structures of nickel(II) and copper(II) complexes with pyrroline N-oxide 2,3-dioxime (H_2L^R) are reported. The ligands show an N,O chelating mode unusual for conventional dioxime ligands. Copper compounds with $Cu_2(HL^R)_2L^R$ composition can be oxidized into complexes containing coordinated vinylnitroxide radicals.

Key words: *dioximes; copper; nickel; vinylnitroxides; crystal structure; magnetic properties*

1. Introduction

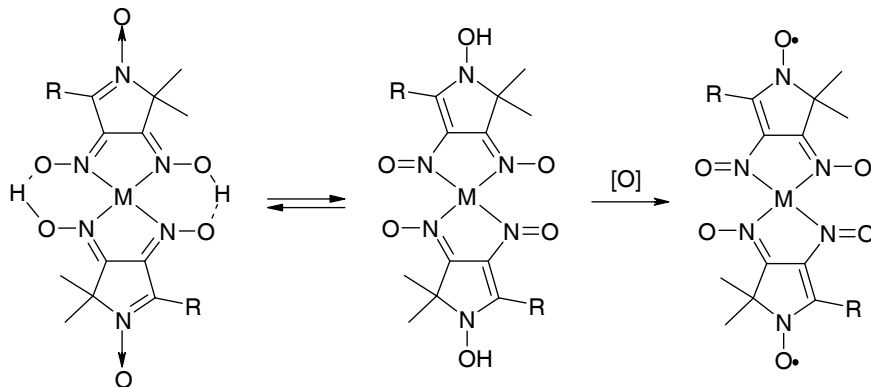
1,2-Dioximes are well-known chelating ligands to transition metal ions and have been under investigation for already almost a century. Most ligands in this class, however, are hydrocarbon derivatives, while heterocyclic 1,2-dioximes are studied quite poorly. We have turned our attention to the derivatives of pyrroline N-oxide H_2L^R (Scheme 1), keeping in mind that complexes of these ligands are promising precursors of coordination polymers, as known for simpler dioximates [1, 2].



Scheme 1. Pyrroline N-oxide H_2L^R

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On the other hand, complexes of H_2L^R dioximes are formally tautomeric with nitrosovinylhydroxylamines, which in turn can be considered as possible ancestors of the very intriguing vinylnitroxide ligands (Scheme 2). It should be noted that the only persistent vinylnitroxide known is derived from the pyrroline-N-oxide skeleton [3].



Scheme 2. Tautomerism between nitrosohydroxylamines and oxime N-oxides

In the present paper, we report the first results obtained on complexes of dioximes H_2L^R with nickel(II) and copper(II).

2. Experimental

The complexes $Cu_2(HL^{Ph})_2L^{Ph} \cdot 4H_2O \cdot EtOH$, $Cu_2(HL^{t-Bu})_2L^{t-Bu} \cdot 4H_2O$, $Ni(HL^{Ph})_2 \cdot 3H_2O$ and $Ni(HL^{t-Bu})_2 \cdot 2.5H_2O$ were obtained by interacting stoichiometric amounts of the reagents in a water–ethanol media (3:2), the pH of the solution being adjusted to 6 with aqueous ammonia. The complexes $CuNa(HL^{Ph})(L^{Ph}) \cdot 4H_2O$, $CuNa(HL^{t-Bu})(L^{t-Bu}) \cdot 5H_2O$, and $CuNa(HL^{Me})(L^{Me}) \cdot 4H_2O$ were obtained similarly, at pH adjusted to 9 with a water solution of Na_2CO_3 . The compounds gave satisfactory elemental analyses; the quantity of the solvent molecules may vary in different preparations, so the compounds are further denoted as solvent-free.

Intensity data for single crystals of complexes were collected on a Smart Apex (Bruker AXS) diffractometer at room temperature using graphite monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). Structures were solved with statistical methods (Bruker-Shelxs) and refined with full-matrix or full-matrix-block least-squares on F^2 (Bruker-Shelxl). The positions of carbon-sitting hydrogen atoms were calculated geometrically and refined isotropically as riding mode. The crystal data and some details of the diffraction experiment are given in Table 1.

The magnetochemical experiment was performed on an MPMS-5S (Quantum Design) SQUID magnetometer at temperatures from 2 K to 300 K with powder samples.

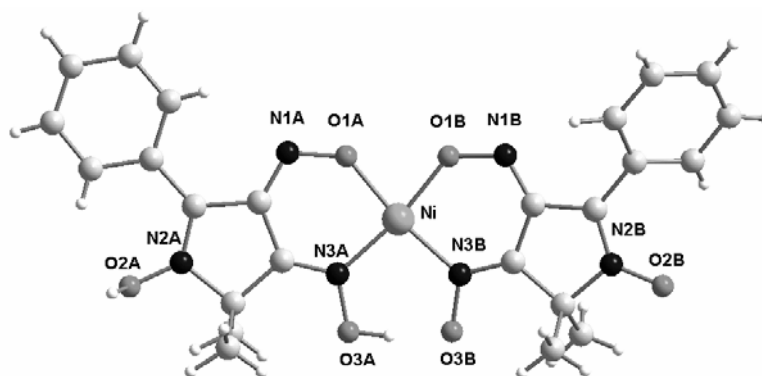
Table 1. Crystal data and X-ray diffraction experiment details for the complexes¹

Crystal data	Compound (solvent molecules omitted)			
	$\text{Cu}_2(\text{HL}^{\text{Ph}})_2\text{L}^{\text{Ph}}$	$\text{Ni}(\text{HL}^{\text{Ph}})_2$	$\text{CuNa}(\text{HL}^{\text{t-Bu}})(\text{L}^{\text{t-Bu}})$	$\text{CuNa}(\text{HL}^{\text{Me}})(\text{L}^{\text{Me}})$
<i>a</i> , Å	11.516(2)	10.645(4)	9.4561(14)	12.3899(12)
<i>b</i> , Å	13.252(4)	10.726(4)	11.2506(17)	13.2043(13)
<i>c</i> , Å	16.876(5)	13.843(5)	13.545(2)	16.1493(17)
α , deg	107.065(6)	81.211(7)	102.925(2)	106.372(21)
β , deg	103.333(6)	76.894(6)	102.831(3)	107.495(16)
γ , deg	96.497(7)	74.140(7)	100.013(2)	95.185(18)
<i>V</i> , Å ³ ; <i>Z</i>	2350(3); 2	1473.7(9); 2	1331.0(3); 2	2131(2); 2
No. of reflections total/unique	10298/6708	6337/4179	5816/3819	5188/2943
GOOF	0.782	0.915	1.075	1.30
<i>R</i> 1	0.0609	0.0488	0.0468	0.0901

¹ Triclinic crystal system, $P\bar{1}$ space group.

3. Results and discussion

Preliminary experiments on the titration of $\text{H}_2\text{L}^{\text{Me}}$ in the presence of copper(II) ions showed that the first and second protons are lost at pH 6 and 9, correspondingly. Therefore, these values were chosen for the preparation of the complexes showing different degrees of deprotonation of the ligand. The acidity was adjusted with aqueous ammonia (pH = 6) and sodium carbonate (pH = 9). At pH = 6, nickel forms complexes with a NiL_2^{R} stoichiometry (R = Ph, t-Bu). The complex with R = Ph (as $\text{Ni}(\text{HL}^{\text{Ph}})_2 \cdot \text{EtOH} \cdot 4\text{H}_2\text{O}$)

Fig. 1. The molecule of $\text{Ni}(\text{HL}^{\text{Ph}})_2$

was investigated by single crystal X-ray diffraction. The specific features of the compound are the N_2O_2 chromophore (Fig. 1), atypical of nickel dioximates [4] and the migration of

one of the oxime protons to the nitron oxygen O2A. The latter circumstance formally converts the nitron into hydroxylamine, however, a N–O(H) bond of 1.30 Å is too short for hydroxylamine, and strong conjugation within the heterocycle does not allow for the assignment of definite bond orders.

Unlike nickel, the copper complexes obtained at pH = 6 have a stoichiometry of $\text{Cu}_2\text{L}_3^{\text{R}}$. According to X-ray diffraction data for $\text{Cu}_2(\text{HL}^{\text{Ph}})_2\text{L}^{\text{Ph}}$ (as $\text{Cu}_2(\text{HL}^{\text{Ph}})_2\text{L}^{\text{Ph}}(\text{H}_2\text{O})_5(\text{EtOH})_2$), the complex is bi-nuclear with bridging oxime oxygens (Fig. 2). All three oxime ligands are coordinated in the N,O chelating mode. Only two oxime hydrogens were localized, which, considered together with charge balance, allows these compounds to be formulated as $\text{Cu}_2(\text{HL}^{\text{R}})_2\text{L}^{\text{R}}$.

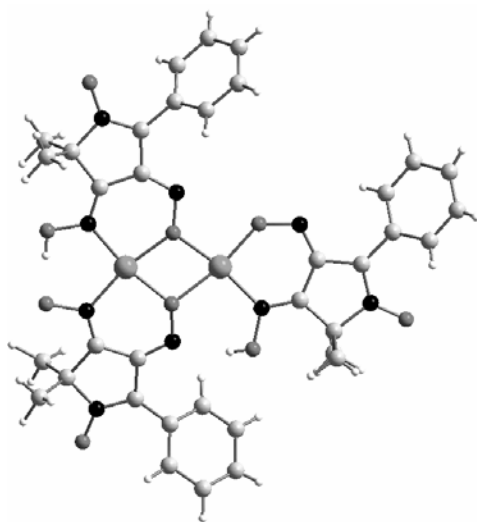


Fig. 2. $\text{Cu}_2(\text{HL}^{\text{Ph}})_2\text{L}^{\text{Ph}}$ fragment

The copper complexes obtained at pH = 9 have a common $\text{CuNaL}_2^{\text{R}}$ ($\text{R} = \text{Ph}$, t-Bu, Me) composition; our attempts to isolate similar complexes of nickel failed. According to X-ray diffraction analysis data for complexes with $\text{R} = \text{t-Bu}$, Me, the materials have a common CuL_2^{R} core, the ligands performing O,N chelating mode. One oxime hydrogen per CuL_2^{R} unit was localized in the $\text{CuNaL}_2^{\text{t-Bu}}$ compound (Fig. 3). This is in accordance with overall composition and results in a $\text{CuNa}(\text{HL}^{\text{R}})\text{L}^{\text{R}}$ unit formula. CuL_2^{R} fragments ($\text{R} = \text{Me}$, t-Bu) are joined in dimers through additional axial contacts, made by copper ions to neighbouring oxime oxygens (Cu–O 2.54(3) Å, $\text{R} = \text{Me}$; 2.47(3) Å, $\text{R} = \text{t-Bu}$; Fig. 4). The supramolecular organization of $\text{CuNa}(\text{HL}^{\text{Me}})\text{L}^{\text{Me}}$ and $\text{CuNa}(\text{HL}^{\text{t-Bu}})\text{L}^{\text{t-Bu}}$ is different: in the former the dimers are isolated and sodium cations form separate tetramers, while in the latter sodium cations are coordinated by oxime oxygens (Fig. 3) and, being additionally bridged by water molecules, give rise to a 1-D coordination polymer (Fig. 5).

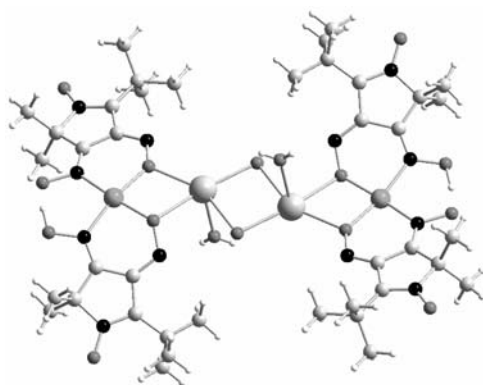


Fig. 3. Cu(HL^{t-Bu})L^{t-Bu} units together with coordinated sodium ions and bridging water molecules

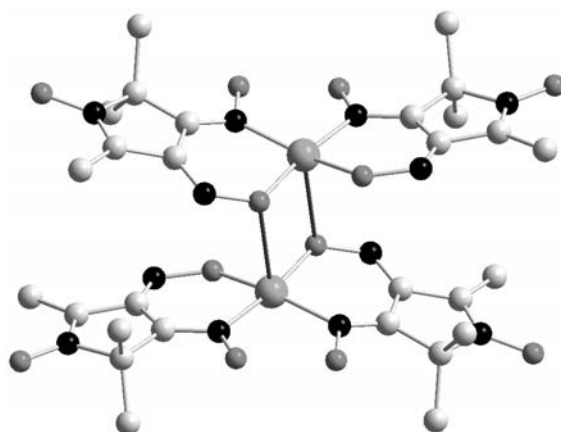


Fig. 4. Dimerization of Cu(HL^R)L^R units

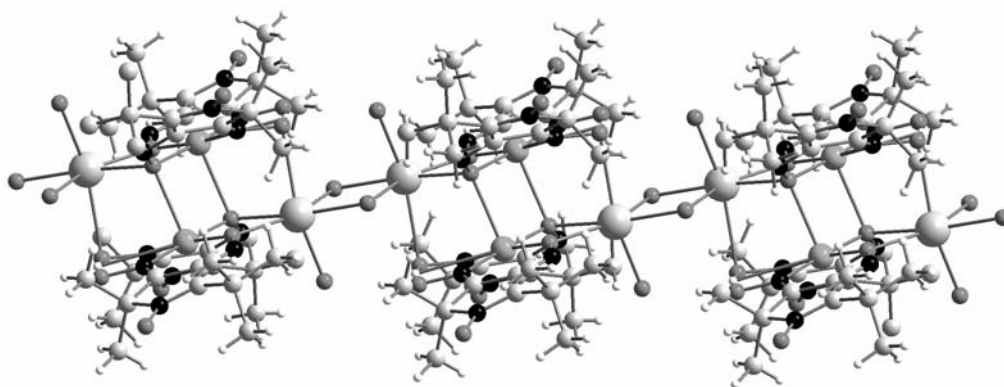


Fig. 5. Coordination polymer CuNa(HL^{t-Bu})(L^{t-Bu})5H₂O, water of crystallization is omitted for clarity

The common feature of all the structurally characterized complexes is the unusual N,O coordination of dioxime, which is very atypical of other known dioximes. The ease of the second deprotonation step of H_2L^R is also noteworthy, which, combined with the tendency to additional coordination demonstrated in $CuNa(HL^{t-Bu})L^{t-Bu}$, makes these complexes promising as linking units between metal ions and opens the possibility for building coordination polymers.

Finally, the presence of "residual" protons makes these complexes potentially liable to oxidation and the formation of corresponding paramagnetic vinylnitroxide-containing species. We have succeeded in oxidizing $Cu_2(HL^R)_2L^R$ ($R = Ph, t-Bu$) compounds: when solutions of these complexes in toluene are treated with PbO_2 (or *m*-nitroperoxobenzoic acid), they demonstrate a change in colour, from brown to deep-blue. The resulting solutions are stable for approximately an hour at ambient conditions; the solvent can be removed by an air stream, avoiding product decomposition provided that the temperature is below 0 °C. The blue resin obtained can be solidified by grinding at 77 K followed by evacuation, the resulting dark-blue solids being stable at -15 °C for several months at least.

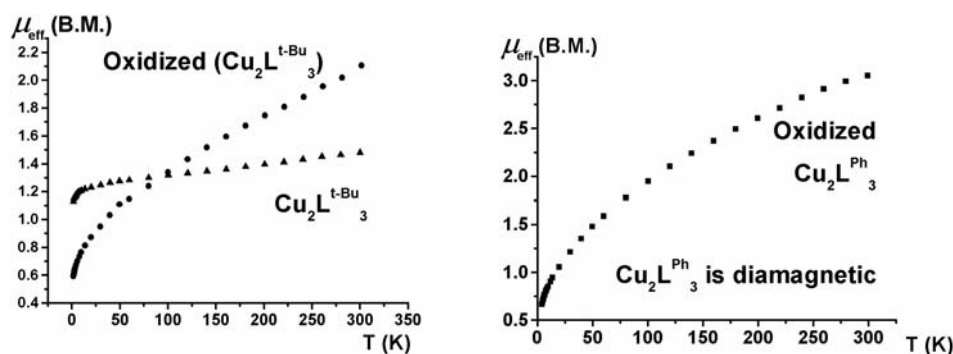


Fig. 6. Magnetic properties of the $Cu_2(HL^R)_2L^R$ complexes and their oxidation products

Figure 6 presents the temperature dependences of magnetic moment for $Cu_2(HL^{t-Bu})_2L^{t-Bu}$ ($Cu_2(HL^{Ph})_2L^{Ph}$ is diamagnetic) and their oxidation products. The data show an increment in magnetic moment for the oxidized compounds (approximately 1 B.M. for $Cu_2(HL^{t-Bu})_2L^{t-Bu}$ and 3 B.M. for $Cu_2(HL^{Ph})_2L^{Ph}$ at 300 K). The magnetic behaviour of the starting complexes is determined by strong antiferromagnetic exchange interactions between the copper(II) ions propagated through the oxygen bridges, this phenomenon being well-documented in literature [5]. This antiferromagnetic exchange is expected to be generally preserved in the oxidation products. On the other hand, the nitroxide spin π -orbital, if nitroxide arises, is antisymmetrical with respect to the plane of the complex, while the copper(II) magnetic orbital, which is of a $d_{x^2-y^2}$ nature, is symmetrical with respect to this plane. Taking into account that the spin of vinylnitroxide must be strongly delocalised over the molecule [3] and therefore interact strongly with the spin of copper, one should expect a very strong exchange of fer-

romagnetic nature in this case. Qualitatively, this is in accordance with the increase in magnetic moment. Unfortunately, the inaccessibility of the high-temperature limit precludes an estimation of the number of spins per formula unit, and the lack of structural information prevents a more detailed interpretation of the magnetic data, therefore further studies are needed. The only doubtless conclusion is that the oxidation of $\text{Cu}_2(\text{HL}^{\text{R}})_2\text{L}^{\text{R}}$ results in the formation of new paramagnetic centres, which we believe to be persistent vinylnitroxide radicals. This is an important result, since normally vinylnitroxides are transient species with lifetimes on the EPR scale. The crucial role of complexation should be stressed here, as the oxidation of $\text{H}_2\text{L}^{\text{R}}$ results in the formation of diamagnetic furoxanes [6].

4. Conclusions

The first results obtained for copper(II) and nickel(II) complexes of pyrroline N-oxide dioximes show that these compounds are structurally quite different from common dioximates, the ligands performing the N,O chelating mode instead of the usual N,N one. The ability of these complexes to easily undergo deprotonation makes them promising candidates for the design of coordination polymers. Finally, copper dioximates with a $\text{Cu}_2(\text{HL}^{\text{R}})_2\text{L}^{\text{R}}$ composition are the precursors of complexes with persistent vinylnitroxides stabilized by complexation.

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Received 16 December 2004

Revised 21 March 2005