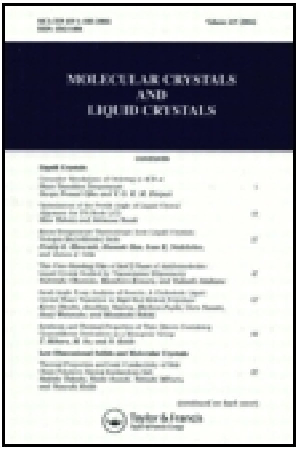

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Metal Complexes of the Nitrile-Substituted Nitroxides

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Version of record first published: 24 Sep 2006

To cite this article: Alexei B. Burdukov, Victor I. Ovcharenko, Dmitrii A. Guschin, Vladimir A. Reznikov, Vladimir N. Ikorskii, Yurii G. Shvedenkov & Natalie V. Pervukhina (1999): Metal Complexes of the Nitrile-Substituted Nitroxides, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 334:1, 395-404

To link to this article: http://dx.doi.org/10.1080/10587259908023337

Mol. Cryst. and Liq. Cryst., 1999, Vol. 334, pp. 395-404
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Metal Complexes of the Nitrile-Substituted Nitroxides

ALEXEI B. BURDUKOV[a], VICTOR I. OVCHARENKO[a], DMITRII A. GUSCHIN[b], VLADIMIR A. REZNIKOV[c], VLADIMIR N. IKORSKII[d], YURII G. SHVEDENKOV[d] and NATALIE V. PERVUKHINA[d]

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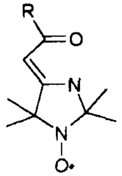
The chelates of the nitrile-substituted 3-imidazoline nitroxides with copper(II), cobalt(II), and nickel(II) have been synthesized and studied with X-ray diffraction and magnetic susceptibility measurements. The influence of the nitrile substituent on structural and magnetic features of the complexes are discussed.

Keywords: nitroxide radicals; transition metal complexes; supramolecular organization; magnetic properties

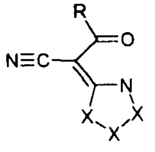
INTRODUCTION

One of the current challenges in the field of metal-nitroxide chemistry is the search of the approaches to the design of 2D and 3D exchange coupled systems capable of manifesting bulk magnetic ordering. Among the supramolecular synthons investigated so far the metal chelates of the 3-imidazoline nitroxide enaminoketones (Scheme 1a) occupy an important position. As the complexes of these ligands provide the connectivity of four at every metal center in a square-planar arrangement, theoretically, they can be used for building both 2D and 3D networks. This approach has successfully been implemented for building 2D coordination and hydrogen bonded metal-nitroxide based polymers [1] while the 3D ones are still to be synthesized.



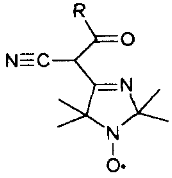
HL^R

a



HL'^R

b



$HL^{CN,R}$

c

Quite recently Saalfrank *et al* has shown that the metal chelates of diamagnetic ligands bearing the nitrile function (Scheme 1b) that are topologically equivalent to the nitroxide complexes in question can be used for building coordination polymers of dimensionality ranging from 1 to 3.[2] These findings have stimulated our interest in the nitrile-substituted paramagnetic ligands similar to that used by Saalfrank (Scheme 1c) and we launched the study of transition metal complexes derived from this type of nitroxide radicals. In the present contribution we describe the first results obtained in the course of our investigations.

EXPERIMENTAL

The ligands $HL^{CN,R}$ were prepared from the corresponding HL^R compounds by NCS chlorination in $CHCl_3$ (purified by silica gel/$CHCl_3$ column chromatography) followed by the substitution of the chlorine by nitrile (NaCN/DMSO).

The following complexes were obtained: $CuL_2^{Me,CN}$, $CuL_2^{i\text{-}Pr,CN}$, $Cu(hfac)L^{Ph,CN}$, $[ML_2^{Ph,CN}(H_2O)_2](EtOH)_2$, $[ML_2^{Ph,CN}(H_2O)](AcOEt)$ (M=Co, Ni), $[ML_2^{CF_3,CN}(H_2O)_2](EtOH)_2$ (M=Co, Ni). These materials were synthesized by reacting the ligand with the corresponding metal salt in water/alcohol media, ammonia being used as the base. No base was used for $HL^{CF_3,CN}$ but the metal acetates were used as the starting materials. The $Cu(hfac)L^{Ph,CN}$ complex was obtained by boiling the mixture of $Cu(hfac)_2$ and the nitroxide in toluene.

The structural data were obtained with an ENRAF-NONIUS CAD-4 machine, SHELX86 and SHELX93 being used for structure solution and refinement.

Magnetic measurements were made with a MPMS-5M SQUID instrument.

RESULTS AND DISCUSSION

Synthetic and structural results

Among the metals investigated, cobalt, nickel, and copper, the latter one behaves significantly differently than the others. The copper chelates precipitate in solvent-free form on recrystallization from different media. The $CuL_2^{Me,CN}$ complex was studied by X-ray diffraction and was found to have a layered polymeric structure. This structure originates from the coordination of nitroxide groups of the $CuL_2^{Me,CN}$ molecule to the copper atoms of the neighboring chelates (Fig. 1, Cu - O 2.47 Å). This type of structure is unknown

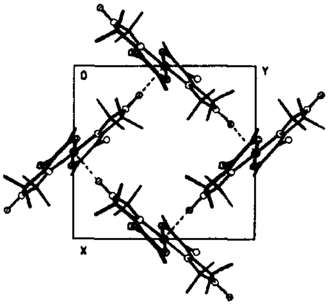


FIGURE 1 The structure of $CuL_2^{Me,CN}$

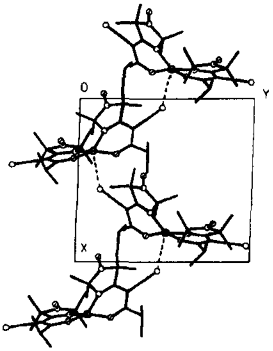


FIGURE 2 The structure of $CuL_2^{i\text{-}Pr,CN}$

for $CuL_2^{Me,H}$ which is molecular [3] but was observed for the copper complexes having an accepting ester function as the R group.[1] Therefore, the formation of the polymeric structure by $CuL_2^{Me,CN}$ seems to result from enhanced Lewis acidity of the chelate which comes out from the electron-withdrawing properties of the nitrile.

The $CuL_2^{i\text{-}Pr,CN}$ complex also possesses a polymeric structure, but the motif is very different from that found in $CuL_2^{Me,CN}$. The copper atom acquires the coordination number of five making a rather weak bond (2.76 Å) to the nitrile of the neighboring chelate, the molecules forming a chain running along the x direction (Fig. 2). Therefore, the bulky iso-propyl substituents disfavor the square-planar conformation of the complex making the layered structure impossible.

Unlike the copper complexes, the nickel and cobalt ones always form solvates. According to structural data, the water molecules incorporated into $[ML_2^{R,CN}(H_2O)_2](EtOH)_2$ are coordinated to the central atom. The resulting $ML_2^{R,CN}(H_2O)_2$ molecules are joined by virtue of hydrogen bonds involving the water and ethanol molecules as well as the nitrile and nitroxide groups. However, despite the similar composition, the hydrogen bonding pattern is very different for the phenyl and trifluoromethyl compounds. In $[ML_2^{Ph,CN}(H_2O)_2](EtOH)_2$ the coordinated water molecules are bound to the nitrile functions of the neighboring chelates (O...N 2.85 Å) related by the x translation (Fig. 3). The other water hydrogen interacts with the ethanol oxygen (O...O 2.75 Å), which, in turn, makes a hydrogen bond to the nitroxide function of the chelate molecule related by the y translation (O...O 2.82 Å). Therefore, the $ML_2^{Ph,CN}(H_2O)_2$ entities are joined into a square grid. In the case of $[ML_2^{CF_3,CN}(H_2O)_2](EtOH)_2$ the water molecules are bound to the nitroxide functions of the neighboring molecules (O...O 2.78 Å) making the layer in the (011) plane (Fig. 4), the layered structures of this type being known for $ML_2^{CF_3,CN}(ROH)_2$.[1] The water molecule is also bound to the ethanol (O...O 2.65 Å) that makes hydrogen bond to the nitrile group of the chelate molecule belonging to the next layer (O...N 2.88 Å). Thus, the layers appear to be cross-linked in the perpendicular direction.

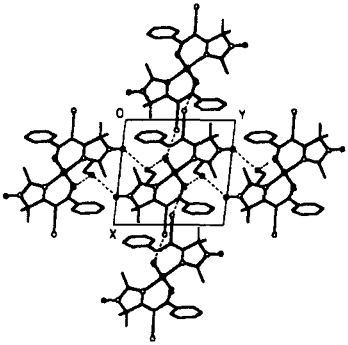


FIGURE 3 The structure of $[ML_2^{Ph,CN}(H_2O)_2](EtOH)_2$

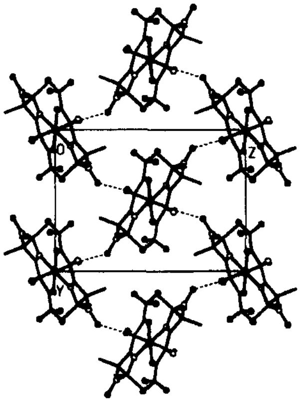


FIGURE 4 The layer in $[ML_2^{CF_3,CN}(H_2O)_2](EtOH)_2$

Considering the role of the nitrile function in the formation of the structures discussed above, two points should be mentioned. First, the nitrile behaves as the electron-withdrawing group, enhancing the Lewis acidity of the metal chelate and providing the coordination of water to the phenyl-substituted complexes. Second, the nitrile function behaves as the hydrogen acceptor giving rise to additional hydrogen bonding.

On transition from $[ML_2^{Ph,CN}(H_2O)_2](EtOH)_2$ to $[ML_2^{Ph,CN}(H_2O)](AcOEt)$ the supramolecular organization of the compounds changes severely. One of the water molecules is removed from the coordination sphere of the metal and is replaced with the nitrile (Ni-N 2.16 Å) coming from the neighboring chelate (Fig.5). As the result, the molecules are joined into zigzag chains running along the y direction. At the same time, the interaction of the water hydrogen with the N-·O group of the neighbor (O...O 2.83 Å) yields the hydrogen bonded chain also directed along the y axis. The chains alter in the x direction and this combination results in the formation of the layer in the (110) plane. Therefore, in the present case the nitrile promotes the coordination of water and also immediately participates in the formation of the coordination bonds.

The structure of $Cu(hfac)L^{Ph,CN}$ gives another example of the coordination bonds formed by the nitrile function. Unlike the previous compounds, the molecules of Cu(hfac)$L^{Ph,CN}$ are asymmetrical: one half of the molecule has two functional groups, the nitrile and the nitroxide, while the other one is "bare". The structure of the compound reveals that both groups are involved in the formation of the net of coordination bonds. The unit cell of the complex contains three independent Cu(hfac)$L^{Ph,CN}$ molecules. In two of them the copper atom acquires the coordination number of six through the bonding to the nitrile and nitroxide groups (Cu-N 2.23, 2.46 Å; Cu-O 2.67, 2.84 Å) while the copper atom of the third molecule is bound to the nitrile only (Cu-N 2.45 Å) and has coordination number 5. In this way the Cu(hfac)$L^{Ph,CN}$ moieties are arranged into a complicated tri-dimensional network (Fig. 6). It should be noted that topologically the Cu(hfac)$L^{Ph,CN}$ fragments are equivalent to $ML^{R,H}$ chelates but the tri-dimensional polymers have not been observed for the latter. The probable reason for Cu(hfac)$L^{Ph,CN}$ to form the tri-dimensional structure is the above-mentioned asymmetry of the molecule.

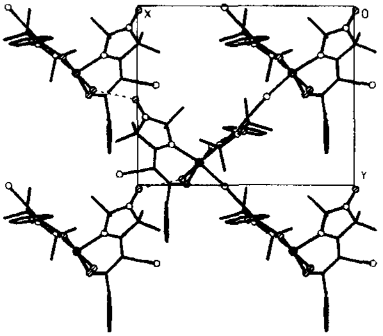


FIGURE 5 The structure of $[ML_2^{Ph,CN}(H_2O)](AcOEt)$

Magnetic properties

While considering the magnetic properties, the contacts between the paramagnetic centers are of primary interest. It's well known from the previous studies that in the 3-imidazoline nitroxide chelates the metal and nitroxide spins are usually coupled in a ferromagnetic way with exchange energy of 10-30 K. [1]

The coupling between the molecules strongly depends on the type of

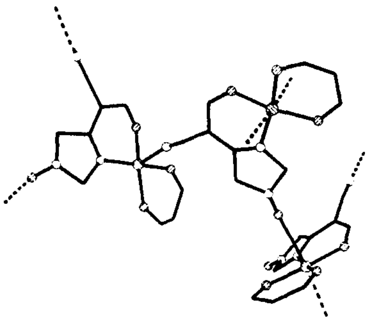


FIGURE 6 The independent fragment in Cu(hfac)$L^{Ph,CN}$, CH_3 and CF_3 being omitted. The dashed lines show the bonds that yield the polymeric structure.

intermolecular interactions. Several types of such interactions are found in the complexes under discussion. They include: i) the coordination bonds with the participation of the nitrile function ($CuL_2^{i\text{-}Pr,CN}$, Cu(hfac)$L^{Ph,CN}$, $[ML_2^{Ph,CN}(H_2O)](AcOEt))$; ii) the hydrogen bonds with the participation of the nitrile function ($[ML_2^{Ph,CN}(H_2O)_2](EtOH)_2$) iii) the coordination bonds with the participation of the nitroxide function ($CuL_2^{Me,CN}$, Cu(hfac)$L^{Ph,CN}$); iv) the hydrogen bonds with the participation of the nitroxide function ($[ML_2^{CF_3,CN}(H_2O)_2](EtOH)_2$). The latter two cases were investigated earlier while the participation of the nitrile is a new feature, so it is necessary to elucidate the possible role of the nitrile function in the propagation of the exchange interactions. The pure case of the metal-to-nitrile bonding is presented by $CuL_2^{i\text{-}Pr,CN}$, although the copper-nitrile separations are rather large (2.76 Å). The magnetic properties of this complex indicate an effective zero-dimensional behavior (Fig. 7) with J=13.2(0.6) K (intramolecular exchange parameter, $H=-2JS_1S_2$) and J'z = -0.4(0.02) K (intermolecular exchange parameter).* The intermolecular exchange is somewhat larger than the values usual for molecular complexes. It should be noted, however, that rather short

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* The fitting of the magnetic data for all the complexes was performed with the software package described in: I.V. Ovcharenko, Yu.G. Shvedenkov, R.N. Musin, V.N.Ikorskii, *Zh.Strukt.Khim*, in press.

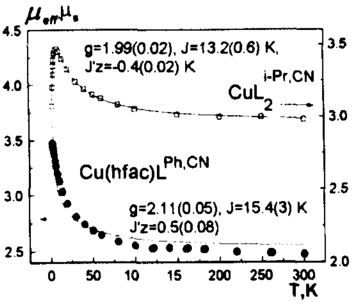

FIGURE 7

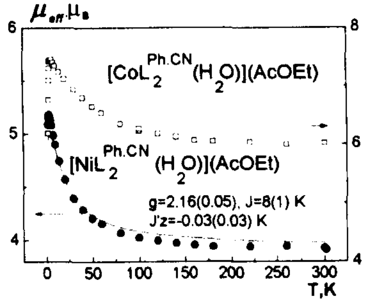

FIGURE 8

N-·O ... O·-N contacts of 3.67 Å are present in the complex, so the J'z parameter cannot be unequivocally attributed to the nitrile exchange pathways. In any way, the exchange interactions are not effectively transferred through the nitrile functions in this case.

The complex Cu(hfac)$L^{Ph,CN}$ presents significantly shorter copper-nitrile contacts of 2.23-2.46 Å along with the long copper-nitroxides bonds (2.67, 2.84 Å). Taking into account the low efficiency of the nitrile exchange pathway in the previous case as well as the fact that nitrile group is axially coordinated to the planar-square copper and, thus, interacts with the non-magnetic d_{z^2} orbital, the exchange through nitrile can be neglected. Under this assumption the polymeric structure splits into separate trimers R-Cu...R-Cu...R-Cu, dashes standing for intramolecular exchange pathways and dots for intermolecular ones. Unfortunately, this magnetic structure is too complicated to be simulated with reasonable accuracy. The attempt to fit the magnetic properties of the complex within the Cu-R dimer model was not very satisfactory and gave J=15(3) K with J'z = 0.5(0.08) K (Fig. 7).

The complex $[ML_2^{Ph,CN}(H_2O)](AcOEt)$ also features the metal-nitrile coordination bonds, now combined with M-O_W-H...O·-N exchange channels. The M-O_W-H...O·-N channels are known to transfer appreciable exchange interactions, and the nitrile pathways can not be excluded from consideration. Therefore, the complex should be treated as chains or grids of R-M-R exchange clusters. Qualitatively, the nickel and cobalt compounds behave in the same way (Fig. 8), thus the nickel one was employed for quantitative analysis. The exchange systems of non-zero dimensionality are difficult to analyze, so we applied the R-Ni-R exchange cluster model and obtained reasonable J=8(1) K and poorly determined J'z=-0.03(0.03) K. The poor simulation of the low-temperature data resulting in low accuracy of J'z indicates that the exchange clusters are not really isolated.

It is of interest that despite the lack of obvious exchange pathways in $[ML_2^{Ph,CN}(H_2O)_2](EtOH)_2$, the magnetic properties of the $[NiL_2^{Ph,CN}(H_2O)_2](EtOH)_2$ also are not correctly simulated within of R-Ni-R cluster model (Fig. 9). The intramolecular exchange has usual value (J=9(1) K) but the low temperature data are not reproduced giving poorly determined and physically unacceptable value of 0.06(0.03) K for the intercluster exchange.

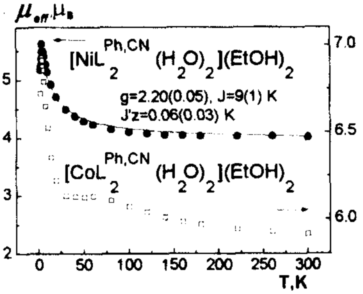

FIGURE 9

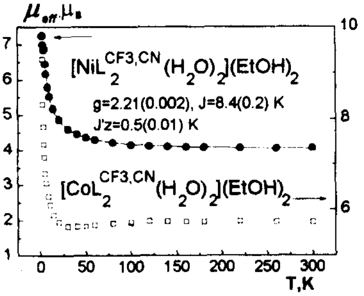

FIGURE 10

The compounds $[ML_2^{CF_3,CN}(H_2O)_2](EtOH)_2$ clearly demonstrate non-zero-dimensional magnetic behavior: the magnetic moment of the complexes increases with the temperature decrease and strongly exceeds the zero-dimensional limit estimated from high-temperature data (Fig. 10). Above 10 K the magnetic properties of the nickel complex are well simulated with the cluster model giving J=8 K and J'z=0.6 K, the data at lower temperatures being not reproduced. Judging from the structure, the compounds should be treated as grids of R-M-R clusters joined by $M-O_W-H...O^{\bullet}-N$ exchange pathways. It is well known that such exchange pathways do transfer antiferromagnetic exchange interaction. In the present case, definitely, the interaction has the ferromagnetic nature.

The complex $CuL_2^{Me,CN}$ has the polymeric structure that is known to result

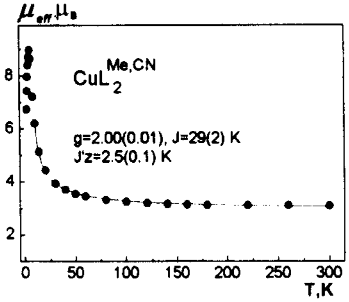

FIGURE 11

into ferromagnetic ordering.[1] As can be seen from Fig. 11, the $CuL_2^{Me,CN}$ does behave in this way. The simulation using the data above 15 K gives a good fit with J=29(2) KI and J'z=2.5(0.1) K, indicating considerable intermolecular interactions of a ferromagnetic nature. The sharp drop of the magnetic moment below 5 K suggests the saturation effect resulting from ferromagnetic ordering.

CONCLUSION

The results of this study show that the introduction of the nitrile function into the of 3-imidazoline nitroxide chelates allowed the building of new supramolecular assemblies based on coordination or hydrogen bonds and brought additional possibilities into crystal engineering of heterospin systems.

Acknowledgments

The financial support from RFBR (grant 96-03-32229) and the Foundation "Integration" is gratefully acknowledged.

References

[1] V. Ovcharenko, A. Burdukov and R. Musin, *Mol. Cryst. Liq. Cryst.*, **273**,88 (1995) and references therein.

[2] R. Saalfrank et al, *Z. Naturforsh.*, **52b**, 125 (1997); *Z. Naturforsh.*, **51b**,399 (1996); *Chem. Ber.*, **125**, 2331 (1992).

[3] N.V. Podberezskaya, G.V. Romanenko, N.V. Pervukhina, *Zh. Strukt. Khim.*, **31**, 99,(1990); V.N. Ikorskii, V.I. Ovcharenko, K.E. Vostrikova et al, *Zh. Neorg. Khim*, **37**, 1177 (1992).