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Studies on Copper(II) Complexes of *o*-Quinone Monooximes. 8.* Penta and Hexacoordinated Adducts of Bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II), [Cu(Clqo)$_2$], with Imidazole and *N*-methylimidazole

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Abstract

Bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II) [Cu(Clqo)$_2$] reacts with imidazole (Im) and with *N*-methylimidazole (MeIm) forming penta and hexacoordinated adducts. The X-ray crystal structure determination showed that the Cu(II) ion is in a distorted trigonal bipyramidal geometry in Cu(Clqo)$_2$·MeIm and in a tetragonally distorted octahedral geometry in Cu(Clqo)$_2$·2L (L = Im, MeIm). In all cases the Clqo quinonic oxygen atoms are in the axial positions while in the parent compound Cu(Clqo)$_2$ they are in the equatorial ones.

IR and electronic spectra were recorded in order to obtain some correlation between structure and spectroscopic features.

Introduction

Interest in copper(II) bis-chelated complexes of *o*-quinone monooximes [referred to as Cu(qo)$_2$] arises from their extensive reactivity [1]. It seems likely that, in all the described reactions, a preliminary step involves the formation of adducts between the potentially basic reagent (and/or the solvent) and the copper(II) center. In order to obtain more information on this subject, a systematic research on Lewis acidity of bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II), [Cu(Clqo)$_2$], taken as a typical exemple of Cu(II) *o*-quinone monooximate, was undertaken in our laboratories, and a number of adducts, with heterocyclic N-bases [1a], halides [1c], methanol [1f], cyanate [1g], were isolated and, when possible, characterized by their X-ray crystal structure determination.

For the pentacoordinated adducts, three square pyramidal [1f, 2, 3a] and one trigonal bipyramidal structures [1g] have been reported. The two known hexacoordinated adducts were found in elongated octahedral geometries [1a, 3b]. The qo ligands occupy the basal positions in the square pyramids and the equatorial positions in the octahedral Cu(qo)$_2$·2CH$_3$CO. In the octahedral Cu(Clqo)$_2$·bpy, the Clqo ligands are distorted from coplanarity due to the severe steric requirements of the bpy molecule. A stereochemistry including square pyramidal and octahedral geometry was found in the trinuclear species [Cu(Clqo)$_2$–I–Cu(Clqo)$_2$–I–Cu(Clqo)$_2$]$^{2-}$ in which the two bridging iodine atoms share the axial positions of a distorted octahedron surrounding the central Cu atom, and the apical positions of the distorted square pyramids surrounding the outer Cu atoms [1c].

In a preceding paper of this series [1a], we reported the synthesis of the 1:1 adduct of Cu(Clqo)$_2$ with imidazole (Im) (and its analogue with benzene in the lattice), and in view of the current interest in the study of Cu(II) complexes with imidazole ligands, we would have liked to determine its molecular structure; however we could not isolate crystals suitable for X-ray determination. Now we have succeeded in obtaining good crystals of the 1:1 adduct with *N*-methylimidazole (MeIm) and we found the Cu(II) center with the unusual trigonal bipyramidal geometry. By using MeIm as the ligand we also obtained the 1:2 hexacoordinated adduct, in which the Clqo quinonic oxygen atoms are unexpectedly displaced by the MeIm ligands from their original equatorial positions [where they are in the parent compound Cu(Clqo)$_2$], to the axial ones. The same feature occurs in the analogous 1:2 adduct with Im.

Besides the molecular structures of these novel copper(II)–imidazole complexes, we report their IR and electronic spectral data, with the aim of obtaining some correlations between the structure and the spectroscopic features.

Experimental

IR spectra were obtained with a 1130 Perkin-Elmer spectrophotometer. Electron absorption spectra were recorded with a Varian Cary 2300 spectrophotometer; the solid state spectra were obtained

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by pasting the samples with nujol and spreading them on strips of filter paper.

$Cu(Clqo)_2$ was prepared following the literature method [4].

Synthesis of the Adducts

$Cu(Clqo)_2 \cdot MeIm$

Bis(4-chloro-1,2-benzoquinone 2-oximato)(*N*-methylimidazole)copper(II) was prepared by stirring an equimolar mixture of $Cu(Clqo)_2$ and MeIm (1 mmol) in MeCN (100 cm^3), for 3 h at room temperature. The crystals were obtained by very slow evaporation of the resulting solution; they were sequentially washed with EtOH and benzene and dried *in vacuo* at room temperature. Melting point (m.p.) 180–182 °C. *Anal.* Calc. for $C_{16}H_{12}Cl_2CuN_4O_4$: C, 41.89; H, 2.64; N, 12.21. Found: C, 41.73; H, 2.62; N, 12.01%.

$Cu(Clqo)_2 \cdot 2Im$ and $Cu(Clqo)_2 \cdot 2MeIm$

These compounds were obtained using the procedure outlined above, using a molar ratio $Cu(Clqo)_2$: ligand = 1:3 and operating in refluxing MeCN.

Bis(4-chloro-1,2-benzoquinone 2-oximato)bis(imidazole)copper(II): decomposition point (d.p.) 120–155 °C. *Anal.* Calc. for $C_{18}H_{14}Cl_2CuN_6O_4$: C, 42.16; H, 2.75; N, 16.38. Found: C, 41.77; H, 2.75; N, 16.39%.

Bis(4-chloro-1,2-benzoquinone 2-oximato)bis(*N*-methylimidazole)copper(II): d.p. 98–115 °C. *Anal.* Calc. for $C_{20}H_{18}Cl_2CuN_6O_4$: C, 44.42; H, 3.35; N, 15.54. Found: C, 44.21; H, 3.20; N, 15.70%.

$Cu(Clqo)_2 \cdot 2NH_3$

This adduct was prepared by bubbling dry NH_3 into a suspension of $Cu(Clqo)_2$ (1 mmol) in MeCN (50 cm^3) for 3 h. The solid residuum was filtered, washed with a small quantity of MeCN and dried at atmospheric pressure and room temperature; in these conditions it loses ammonia in a few days; *in vacuo* it decomposes in a few hours reverting to $Cu(Clqo)_2$. *Anal.* Calc. for $C_{12}H_{12}Cl_2CuN_4O_4$: C, 35.09; H, 2.94; N, 13.64. Found: C, 35.09; H, 2.87; N, 13.56%.

Molecular Structure Determinations

Crystal data were recorded on a CAD 4 diffractometer. For experimental practice and pertinent details for $Cu(Clqo)_2 \cdot MeIm$ (**1**), $Cu(Clqo)_2 \cdot 2Im$ (**2**) and $Cu(Clqo)_2 \cdot 2MeIm$ (**3**), see 'Supplementary Material'. The final *R* factors were found to be: 5.1% (R_w, 5.0%) for complex **1**; 4.0% (R_w, 4.3%) for complex **2** and 3.9% (R_w, 4.2%) for complex **3**. Selected bond distances and angles appear in Tables I, II and III.

TABLE I. Selected Bond Distances (Å) and Angles (°) for $Cu(Clqo)_2 \cdot MeIm^a$

Cu–N(1)	2.038(6)	Cu–N(3)	1.989(6)
Cu–N(2)	1.963(5)	Cu–O(2)	1.978(5)
Cu–O(4)	2.138(3)		
N(1)–O(1)	1.246(8)	N(3)–O(3)	1.250(7)
N(1)–C(1)	1.398(9)	N(3)–C(11)	1.358(7)
O(2)–C(2)	1.285(8)	O(4)–C(12)	1.269(9)
N(3)–Cu–O(2)	169.6(2)	N(2)–Cu–N(1)	138.3(2)
N(3)–Cu–N(2)	97.2(2)	O(4)–Cu–N(1)	93.4(2)
N(3)–Cu–O(4)	80.2(2)	O(2)–Cu–N(2)	93.0(3)
N(3)–Cu–N(1)	92.3(2)	O(2)–Cu–O(4)	91.7(2)
N(2)–Cu–O(4)	128.2(2)	O(2)–Cu–N(1)	81.6(3)

[a] e.s.d.s given in parentheses.

TABLE II. Bond Distances (Å) and Selected Bond Angles (°) for $Cu(Clqo)_2 \cdot 2MeIm$

Cu–O(4)	2.365(7)	N(5)–C(17)	1.393(6)
Cu–O(2)	2.329(5)	N(5)–C(19)	1.354(6)
Cu–N(1)	2.030(4)	N(6)–C(17)	1.384(5)
Cu–N(2)	2.038(4)	N(6)–C(18)	1.281(7)
Cu–N(3)	2.016(3)	N(6)–C(20)	1.455(7)
Cu–N(5)	1.985(4)	C(1)–C(2)	1.440(8)
Cl(1)–C(5)	1.745(6)	C(1)–C(6)	1.457(7)
Cl(2)–C(11)	1.743(6)	C(2)–C(3)	1.416(8)
O(1)–N(1)	1.217(5)	C(3)–C(4)	1.506(9)
O(2)–C(2)	1.283(6)	C(4)–C(5)	1.399(9)
O(3)–N(2)	1.303(5)	C(5)–C(6)	1.248(8)
O(4)–C(8)	1.214(7)	C(7)–C(8)	1.479(7)
N(1)–C(1)	1.390(6)	C(7)–C(12)	1.419(7)
N(2)–C(7)	1.295(6)	C(8)–C(9)	1.479(8)
N(3)–C(13)	1.237(6)	C(9)–C(10)	1.148(9)
N(3)–C(15)	1.393(6)	C(10)–C(11)	1.51(2)
N(4)–C(13)	1.308(5)	C(11)–C(12)	1.447(9)
N(4)–C(14)	1.448(7)	C(14)–C(15)	1.324(6)
N(4)–C(16)	1.477(6)	C(18)–C(19)	1.388(6)
O(2)–Cu–O(4)	178.5(1)		
O(2)–Cu–N(1)	78.3(1)	O(4)–Cu–N(1)	103.2(2)
O(2)–Cu–N(2)	104.1(2)	O(4)–Cu–N(2)	74.4(1)
O(2)–Cu–N(3)	92.8(1)	O(4)–Cu–N(3)	87.5(1)
O(2)–Cu–N(5)	88.2(1)	O(4)–Cu–N(5)	91.6(1)
N(1)–Cu–N(2)	177.5(1)	N(2)–Cu–N(3)	91.2(1)
N(1)–Cu–N(3)	89.5(1)	N(2)–Cu–N(5)	89.9(1)
N(1)–Cu–N(5)	89.4(1)	N(3)–Cu–N(5)	178.3(2)

[a] e.s.d.s given in parentheses.

Results and Discussion

$Cu(Clqo)_2 \cdot MeIm$

Copper(II) ion is surrounded by five donor atoms in a distorted trigonal bipyramidal stereochemistry (Fig. 1). The extent of distortion towards square pyramidal stereochemistry may be evaluated as 13.5% by comparing the dihedral angles of the theoretical and the experimental polyhedra [5].

TABLE III. Bond Distances (Å) and Bond Angles (°) for Cu(Clqo)$_2\cdot$2Im[a]

Cu–O(2)	2.369(4)	Cu–N(2)	1.994(5)
Cu–O(4)	2.401(3)	Cu–N(3)	1.985(6)
Cu–N(1)	2.044(6)	Cu–N(5)	2.022(6)
N(1)–O(1)	1.18(1)	N(2)–O(3)	1.31(1)
N(1)–C(1)	1.40(1)	N(2)–C(7)	1.35(1)
O(2)–C(2)	1.34(1)	O(4)–C(8)	1.17(1)
C(1)–C(2)	1.31(2)	C(7)–C(8)	1.55(1)
C(2)–C(3)	1.48(1)	C(8)–C(9)	1.44(1)
C(3)–C(4)	1.45(2)	C(9)–C(10)	1.27(2)
C(5)–C(6)	1.22(1)	C(11)–C(12)	1.44(1)
C(6)–C(1)	1.55(1)	C(12)–C(7)	1.33(1)
Cl(1)–C(5)	1.757(7)	Cl(2)–C(11)	1.732(7)
N(3)–C(13)	1.37(1)	N(5)–C(16)	1.27(1)
C(13)–N(4)	1.32(1)	C(16)–N(6)	1.37(1)
N(4)–C(14)	1.30(1)	N(6)–C(18)	1.45(1)
C(14)–C(15)	1.47(1)	C(18)–C(17)	1.25(1)
C(15)–N(3)	1.42(1)	C(17)–N(5)	1.35(1)
O(2)–Cu–O(4)	178.7(2)	O(4)–Cu–N(1)	103.6(2)
O(2)–Cu–N(1)	77.6(2)	O(4)–Cu–N(2)	74.3(2)
O(2)–Cu–N(2)	104.5(2)	O(4)–Cu–N(3)	89.8(2)
O(2)–Cu–N(3)	90.6(2)	O(4)–Cu–N(5)	90.2(2)
O(2)–Cu–N(5)	89.4(2)	N(2)–Cu–N(3)	93.0(2)
N(1)–Cu–N(2)	177.0(3)	N(2)–Cu–N(5)	87.5(2)
N(1)–Cu–N(3)	89.0(2)	N(3)–Cu–N(5)	179.5(2)
N(1)–Cu–N(5)	90.6(2)		

[a] e.s.d.s given in parentheses.

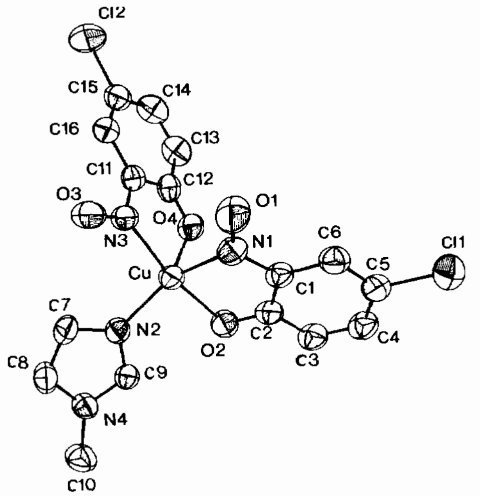

Fig. 1. ORTEP view of Cu(Clqo)$_2\cdot$MeIm.

The equatorial plane is formed by two nitrogen atoms [the imidazolic N(2) and the oximic N(1)] and one oxygen atom [the quinonic O(4)]; the axial positions are thus occupied by a nitrogen and an oxygen atom [(the oximic N(3) and the quinonic O(2)]. This geometry is unusual; in fact neutral copper(II) bischelated complexes tend to increase their coordination number maintaining the square arrangement of the chelating ligands around the metal center, thus adopting an apically elongated square pyramidal geometry for the pentacoordination and a tetragonally elongated octahedral geometry for the hexacoordination [6]. This behaviour has been generally found in all the Cu(qo)$_2$ adducts with monodentate ligands examined so far; the only other case of trigonal bipyramidal stereochemistry is shown by the anionic species [Cu(Clqo)$_2$NCO]$^-$ [1g]. It is not clear why the Cu(Clqo)$_2\cdot$MeIm adduct is more stable in TBP than in SP geometry. A good reason might be found in the noticeable ligand strength of MeIm which, as it comes very intimately into the coordination sphere of the copper(II) ion, displaces an oxygen atom from the square plane. Moreover, a solvent effect cannot be ruled out; in fact it has been recently reported that two isomeric forms (SP and TBP) of the same pentacoordinated copper(II) complex have been crystallized from different solvents [7]. The copper(II) center is slightly shifted [0.0359(2) Å] out of the equatorial plane towards O(2); neither does it lie on the planes formed by the Clqo ligands, being shifted 0.282(2) Å out of the plane of one of them and 0.137(2) Å out of the other one. An unusual large distance is found from the MeIm plane [0.662(2) Å]. The bond distances around Cu(II) are in agreement with the values observed in the other Cu(qo)$_2$ derivatives, except the Cu–O(4) bond which is significantly longer; the Cu–N(2) bond length compares well with the values reported for the other Cu(II) complexes of imidazole or imidazole derivatives [8].

Cu(Clqo)$_2\cdot$2MeIm and Cu(Clqo)$_2\cdot$2Im

These adducts have quite similar molecular structures. The coordination polyhedra are elongated rhombic octahedra (Figs. 2 and 3). The equatorial vertices are occupied by four nitrogen atoms, *i.e.* the N atoms of the two imidazole ligands (in *trans* position) and the oximic N atoms of the two Clqo ligands; thus the axial positions are taken by the quinonic oxygen atoms. As in the case of the 1:1 MeIm adduct, the quinonic oxygen atoms have been displaced, by the imidazole ligands, from their original equatorial positions. Consequently a dramatic lengthening of the Cu–O bonds, with respect to all the other Cu(qo)$_2$ derivatives is observed. The copper(II) centers are slightly shifted out of the equatorial planes towards O(2), [0.0411(1) Å for complex 2 and 0.0055(1) Å for complex 3]. In both complexes the planarity of the quinone monooximic parent chromophore, N(1)N(2)O(2)O(4), is maintained. The MeIm ligands in complex 2, and the Im ligands in complex 3 are coplanar. The Clqo ligands, coplanar in complex 2, are slightly distorted from coplanarity in complex 3; this latter feature likely depends on the strong hydrogen bonds between the two imidazolic hydrogen atoms of a molecule and the quinonic oxygen atoms of the

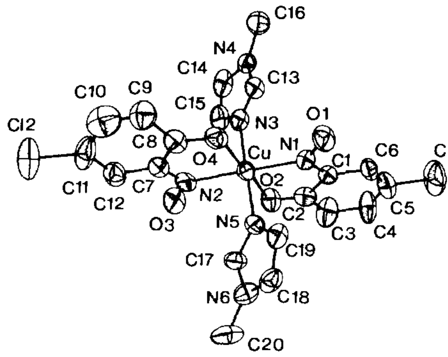

Fig. 2. ORTEP view of Cu(Clqo)$_2$·2MeIm.

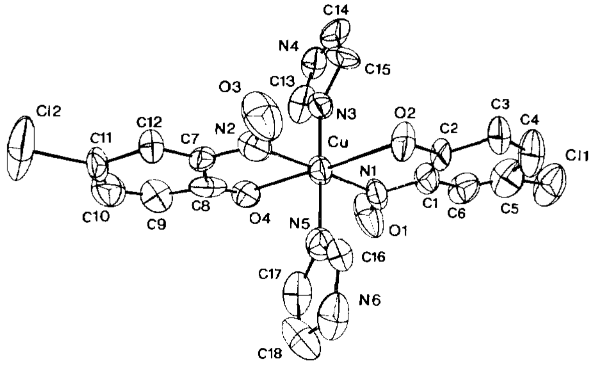

Fig. 3. ORTEP view of Cu(Clqo)$_2$·2Im.

nearest ones. Actually, if $i = x, 1 - y, 1/2 + z$, H-(Im1)–O(2)^i = 1.83(1) Å and the angle N(4)–H-(Im1)–O(2)^i is 152.3(4)°; and if $ii = x, -y, -1/2 + z$, HIm2)–O(4)^{ii} = 1.88(1) Å and the angle N(6)–H(Im2)–O(4)^{ii} is 143.5(3)°.

It seems worthwhile to notice that Im and MeIm behave, towards Cu(qo)$_2$, as remarkably stronger ligands than pyridine. In fact with pyridine, the 1:2 adduct cannot be obtained, and in the 1:1 adduct the N-py atom is situated in the apical position of an elongated square pyramid. The properties of the imidazole ring as ligand derive from both its σ donor and π-electron acceptor capability [8]. In order to verify which factor is dominant in the present case, we extended the comparison to NH$_3$ which has not π acceptor character. The hexacoordinated adduct Cu(Clqo)$_2$·2NH$_3$ was obtained; although its crystal structure could not be determined, owing to the extremely small size of the obtained crystals, it can be seen from IR spectral data (*vide infra*), that the chelated rings are very similar to those of the octahedral adducts **2** and **3** (*i.e.* with quite long Cu–O bonds). Thus it seems likely that, at least in this case, the behaviour of Im and MeIm is essentially due to their Lewis base character.

A comparison of the Cu–O bond distances in the Im and the MeIm adducts, shows that the bond lengthening is greater in the first case, which is consistent with the higher basicity of Im compared to MeIm and to the above mentioned hydrogen bonds. The tetragonality parameters (0.84 and 0.85 respectively) do not allow a clear discrimination between a static or a dynamic behaviour of the $N_2N'_2O_2$ chromophore [9].

An intriguing feature of these adducts consists in the anomalous bond lengths and angles observed with the Clqo ligands. In fact in all the other described structures a clearly oximic behaviour was found, with long and short bonds regularly alternating through the rings; therefore we expected to find the same trend, or possibly all the C–C bond distances almost equal, indicative of a nitrosophenolic behaviour of the Clqo ligands. Instead in the present adducts neither behaviour is found; moreover noticeable differences of the corresponding bond lengths occur between the two Clqo ligands and the two imidazole rings.

Vibrational and Electronic Spectra

The IR spectra of Cu(Clqo)$_2$·2Im, Cu(Clqo)$_2$·2MeIm and Cu(Clqo)$_2$·MeIm have been examined in comparison with those of the parent compound Cu(Clqo)$_2$ and its adducts of known structure. The most characteristic features concern the C=O and the C=N stretching frequencies of the qo ligand [10], which are found at increasing energies along this series: Cu(Clqo)$_2$, Cu(Clqo)$_2$·bpy, Cu(Clqo)$_2$·2NH$_3$, Cu(Clqo)$_2$·2Im, Cu(Clqo)$_2$·2MeIm (Table IV).

Recently we observed that a shift of C=O and C=N stretching frequencies to higher values occurs when the Clqo species behaves as a non-chelated ligand, for instance in KClqo (ν(C=O) 1620 cm^{-1}; ν(C=N) 1550 cm^{-1}); in fact in this case the amount of electron delocalization through the –O=C–C=N–O– chain decreases, and the C=O and C=N bond order increases [1d]. In the octahedral adducts the additional ligands displace the Clqo from the equatorial plane causing a noticeable lengthening of the Cu–O bond; the effect on the electron delocalization through the chelated ring and on the C=O and C=N

TABLE IV. IR Spectra of Selected Cu(Clqo)$_2$ Derivatives in the C=O and C=N Stretching Regions

	Cu(Clqo)$_2$	Cu(Clqo)$_2$·bpy	Cu(Clqo)$_2$·2NH$_3$	Cu(Clqo)$_2$·2Im	Cu(Clqo)$_2$·2MeIm
ν(C=O) (cm^{-1})	1590	1605	1615	1615	1615
ν(C=N) (cm^{-1})	1520	1530	1535	1530	1530–1550

bond order is similar (although less intense) to the loss of the chelation. Also in the case of $Cu(Clqo)_2 \cdot 2NH_3$, the IR spectrum points to a quite similar feature. Instead, when the additional ligands are in the apical position of an elongated square pyramid [for instance $Cu(Clqo)_2 \cdot MeOH$, $Cu(Meqo)_2 \cdot Py$], or in the axial positions of an elongated octahedron [for instance $3Cu(Clqo)_2 \cdot 2KI$], the chelation of the qo ligands is not altered and no shift is observed.

In the case of $Cu(Clqo)_2 \cdot MeIm$, a C=O group is displaced from its original position to an axial vertex but, the coordination polyhedron being a compressed trigonal bipyramid, the Cu–O bond length does not change greatly and no shift of the C=O and C=N stretching occurs. Instead a clear splitting of the C=O band is observed; perhaps it might be related to the stereochemically non-equivalent positions of the two C=O groups.

The electronic spectra of the described imidazole and methylimidazole adducts in acetonitrile are identical with the spectrum of $Cu(Clqo)_2$ in the same conditions, indicating that these adducts are unstable and revert to the parent compound at concentrations suitable for such measurements. However significant differences appear in the solid state spectra. The Vis spectrum of solid $Cu(Clqo)_2$ is characterized by a broad band centered at 580 nm; this band shifts to 530 nm in solution. Since $Cu(Clqo)_2$ is reported [4] to be polymeric (and thus octahedral) in the solid state and dimeric (and thus presumably square pyramidal) in solution, this shift is consistent with the increase of tetragonal distortion of the chromophore. The same trend is found in the solid state spectra in going from $Cu(Clqo)_2$ to the octahedral adducts $Cu(Clqo)_2 \cdot byp$, $Cu(Clqo)_2 \cdot 2Im$ and $Cu(Clqo)_2 \cdot 2MeIm$, in which the Cu(II) d–d bands are centered at 545, 540, 535 nm respectively. The slight increase of the shift along the series might be related to the slight increase of the tetragonality of the $N_2N'_2O_2$ chromophore in these adducts.

Supplementary Material

Experimental details and full listing of data concerning the crystal structures are available from the authors on request.

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