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Steric Effects of Nonbonded Interligand Interactions in Dimeric Adducts, Ni(II) Quinaldinetrimethylacetate and Cu(II) Acridinetrimethylacetate

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The structures of two dimeric complexes of the type $[LM(OOCR)_2]_2$*,* $QNi(OOCCMe_3)_4NiQ$ *(I) where Q is quinaldine, and* $ACu(OOCCMe_3)_4CuA$ *(II) where A is acridine, have been studied by X-ray diffraction (an automatic diffractometer, anisotropic LS treatment, λ-Cu for I and λ-Mo for II). Our purpose was to determine structural consequences of the combined action by steric hindrances due to α-substituted pyridine ligands and electronic effects of tert-butyl substituents in the carboxylate bridges. The crystals I are triclynic,* $P\bar{1}$, $a = 11.168(2)$, $b = 18.334(2)$, $c = 11.452(3)$ Å, $\alpha = 90.037(4)$, $\beta = 119.01(1)$, $\gamma = 89.06(4)^\circ$, $Z = 2$. *The Ni···Ni distance of 2.754(3) Å is considerably larger than it is in low-spin clusters containing Ni. The Ni atoms are displaced by 0.23 Å from the plane containing four oxygen atoms towards the ligands Q. The Ni–N bond has the usual length, 2.07 Å, and makes an angle of 10° with the Ni–Ni axis. The crystals II are triclynic,* $P\bar{1}$, $a = 9.448(4)$, $b = 11.463(5)$, $c = 11.963(4)$ Å, $\alpha = 105.61(3)$, $\beta = 103.40(3)$, $\gamma = 105.92(3)^\circ$, $Z = 1$. *The Cu···Cu distance is of 2.702(1) Å. The Cu atoms are displaced by 0.24 Å from the oxygen plane towards A. The normal intramolecular contacts are maintained owing to Cu–N bond elongation to 2.371 Å.*

Introduction

As shown in the recent X-ray studies [1, 2] of antiferromagnetic dimers $LCu(OOCR)_4CuL$ where L is a substituted pyridine ligand, the introduction of an α-substituent into L (as in α-picoline or quinoline) noticeably affects the dimer structures. The effect is unusually large displacement of the Cu atoms from the plane containing four oxygen atoms which prevent the formation of too short nonbonded contacts $C_L(\alpha)\cdots O_{OOCR}$. Accordingly, the Cu···Cu distances increase to 2.72–2.75 Å [1, 2]. Similar features are observed in the structure of the antiferromagnetic dimer, Co(II) quinolinedibenzoate (Co···Co of 2.83 Å) [3]. We have already stated that interligand interactions may favour the dimerization itself: steric hindrances to the addition of one more ligand L make the dimeric 'lantern'-type structure $[LM(OOCR)_2]_2$ more feasible than monomeric or polymeric structures of the type $[L_2M(OOCR)_2]_n$ [4].

This idea was in fact realized in intended synthesis of dimeric complexes of the first transition row elements (Mn, Co, Ni) which show preference for the formation of regular octahedrons. Thus, α-substituted pyridines (α-picoline, quinoline, quinaldine) were used to synthesize 'lantern'-structured dimeric Mn(II) and Co(II) carboxylates earlier unknown (R = Ph, m-FC_6H_4, m-ClC_6H_4, m-$CH_3OC_6H_4$, C_4H_3O, C_4H_3S) [4, 5]. Pyridine ligands free of α-substituents (pyridine, γ-picoline) reacted to give $L_2M(OOCR)_2$ under the same conditions [4, 6]. On the other hand, increase in electron density on M due to the presence of the strong electron donor, CMe_3, as substituent in the carboxylate ligand, also favours the formation of $LM(OOCR)_2$ fragments rather than $L_2M(OOCR)_2$. Dimeric antiferromagnetic carboxylate adducts of Mn, Fe, Co and Ni may then be prepared even in the absence of α-substituents on the pyridine ring [6, 7]. It should however be noted that with Ni(II), both the use of α-substituted pyridines and the presence of CMe_3 groups in the carboxylate ligands are recommended as neither of the conditions mentioned can alone guarantee the formation of dimers. Thus, with α-picoline or quinoline for L, the complexes $L_2Ni(OOCR)_2$ are only formed if R is Me, Ph, 4-ClC_6H_4 and 2-$NO_2C_6H_4$ [8], and with CMe_3 for R if L is γ-picoline [7]. The latter reaction goes likewise with Cu(II).

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We deemed it interesting to study the structure effects due to the combined action by both dimer-stabilizing factors, *viz.* the presence of α-substituents in the pyridine ligands and electron releasing CMe_3 groups in the carboxylato bridges. We have chosen di-α-substituted pyridine ligands whose structure effects should be most manifest. Structures of Cu(II) carboxylates containing such ligands have not been studied thus far; as for Ni(II), only two its 'lantern'-structured dimers are at all known: $Ni_2(S_2CR)_4$ where R may be $PhCH_2$ or Me (recently, their structures have been determined by X-ray diffraction [9]).

In this work we describe the results of an X-ray diffraction study of $QNi(OOCCMe_3)_4NiQ$ (I) where Q is quinaldine and $ACu(OOCCMe_3)_4CuA$ (II) where A is acridine.

Results

Green crystals I were obtained as recommended in [6]. The crystals are triclynic, $P\bar{1}$. The unit cell contains two independent dimeric species. The structure of the centrosymmetric complex I together with mean bond length and valence angle values (averaged over two independent molecules with centres of symmetry at 0,0,0 and 1/2,1/2,0) are represented in Fig. 1. The metal coordination polyhedron is a square pyramid with planar quinaldine ligand in the axial position and four oxygen atoms of planar carboxylato bridges forming its base (the mean ONiO and ONiN angle values are 88.1(4) and 98.5(5)°, respectively). The Ni–N bond 2.07 Å long forms an angle of 10° with the Ni•••Ni axes and is bent towards the C(8) atom. This is probably due to the mutually balanced action by the short intramolecular contacts O(1)•••CH_3 (Q), 2.89 Å, O(4′)•••CH_3 (Q), 3.00 Å, on the one hand and O(3)•••C(8), 3.06 Å, O(2′)•••C(8), 3.18 Å, on the other. The Ni•••Ni distance, 2.754(3) Å, is considerably larger than the Ni–Ni bond length in a number of low-spin clusters (*ca.* 2.4 Å [10]) and in nickel metal (2.492 Å). It thus appears to be a nonbonding distance.

The second compound studied, complex II, was made like other copper carboxylates of the composition $LCu(OOCCMe_3)_4CuL$ [6]:

$$[Me_3CCOOH{\cdot}Cu(OOCCMe_3)_2]_2 + 2A \xrightarrow[\text{toluene}]{20^\circ} ACu(OOCCMe_3)_4CuA$$

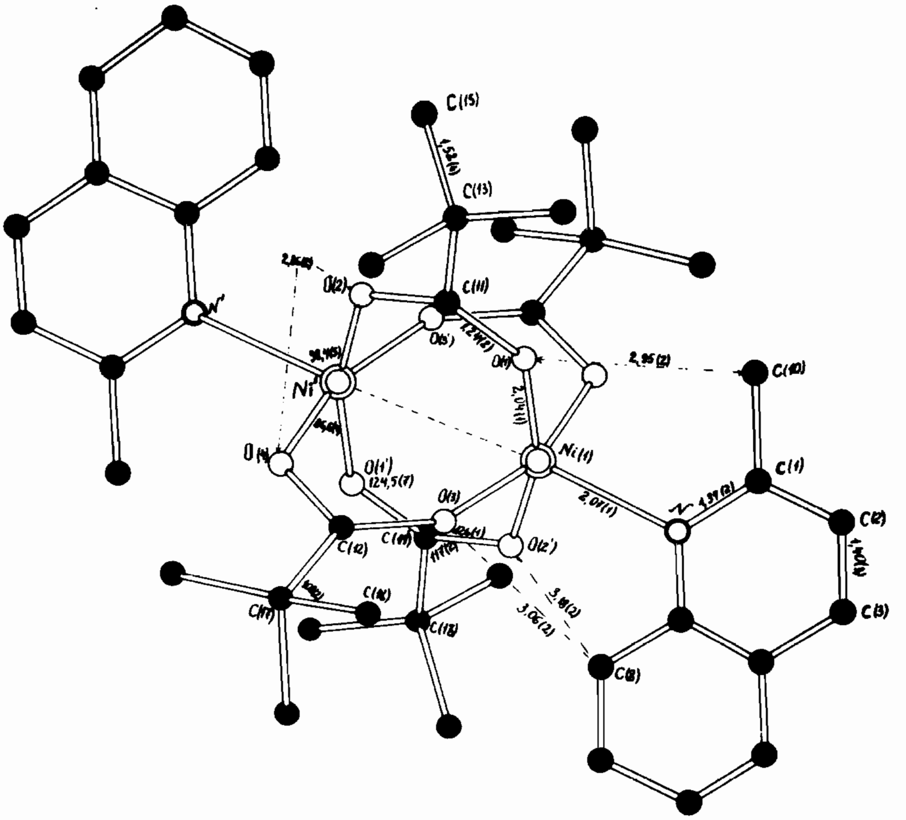

Fig. 1. The structure of $[C_{10}H_9N{\cdot}Ni(OOCCMe_3)_2]_2$ (I).

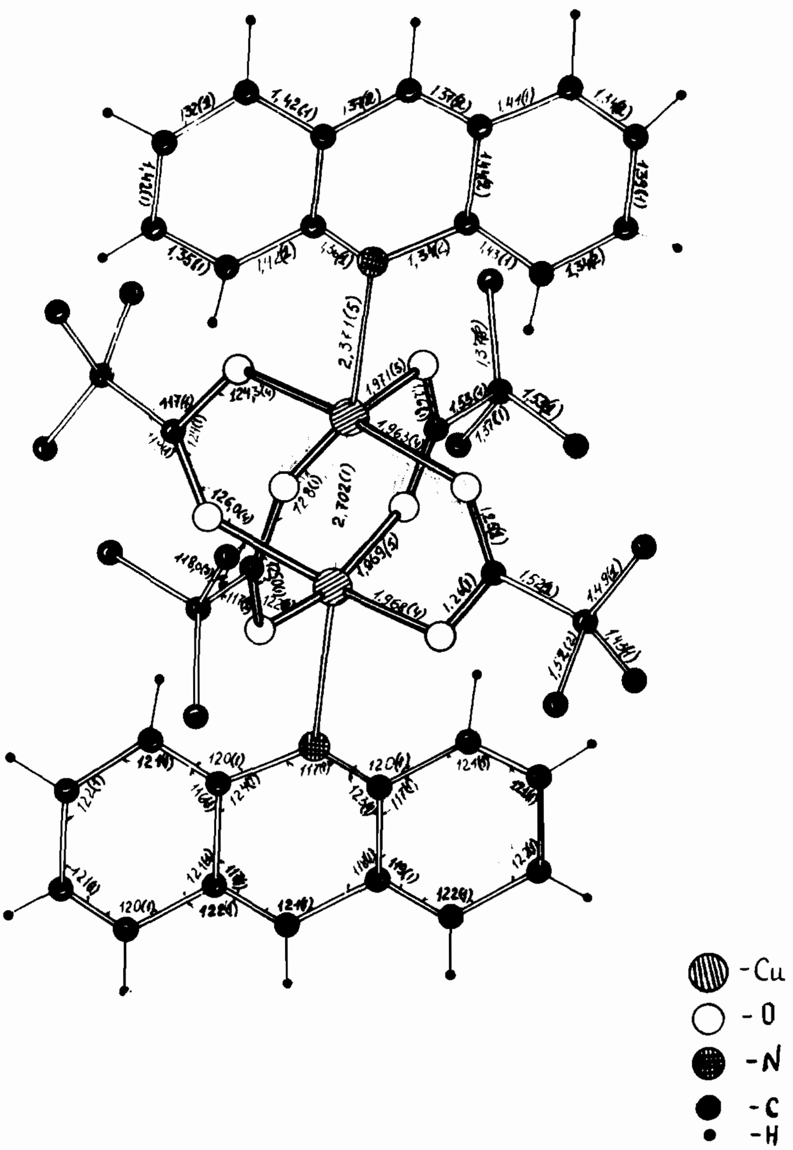

Fig. 2. The structure of $[C_{13}H_9N \cdot Cu(OOCCMe_3)_2]_2$ (II).

The complex $A_2Cu(OOCCMe_3)_2$ does not occur in that reaction (A is acridine). Green crystals II are also triclynic, space group $P\bar{1}$, but contain only one dimeric molecule per unit cell. The structure of II is shown in Fig. 2 together with average bond length and valence angle values.

Like in complex I, planar axial ligands in II lie in near bisector planes of the dihedral angles between planar carboxylato ligands and make practically equal angles with the latter. The symmetrical structure of acridine ligands results in that the Cu–N bond (2.371 Å) is almost collinear with the Cu···Cu axis (the CuCuN angle is equal to 177°). The molecular symmetry is nearly D_{2h}. The Cu–O bonds are essentially shorter than the Ni–O bonds in I (the respective average values are 1.965 and 2.01 Å). The Cu···Cu distance in II is also shorter somewhat than the Ni···Ni distance in I (2.702 against 2.754(3) Å). The other characteristics of the central unit in II are near those of I: the Cu atoms are displaced from the oxygen square plane by 0.24 Å, the average carboxylato C–O and C–C bond lengths are equal to 1.26 and 1.53 Å; the OCuO and OCuN, OCO and CuOC angles are equal to 89.18 and 96.9, 124.4 and 125.1°, respectively.

Discussion

The most important feature of the structures of I and II is the absence of direct Ni–Ni and Cu–Cu bonds. As a result, spin–spin interactions only involve the bond system of carboxylato bridges. Closer approach of Ni atoms to each other in I is hindered by the short (of *ca.* 3.0 Å) intramolecular contacts between the carboxylato oxygen atoms and quinaldine C atoms. The difference in the nature of Ni–Ni interactions between antiferromagnetic complex I (the exchange parameter value, –2J, is equal to 320 cm^{-1}) and diamagnetic dimer $Ni_2(S_2CCH_2Ph)_4$ [9] is most manifest. The Ni atoms in I are displaced by 0.23 Å towards apical ligands from the oxygen plane, whereas in $Ni_2(S_2CCH_2Ph)_4$, the formation of the direct Ni–Ni bond (2.551(3) Å) responsible for diamagnetism is accompanied by 0.13 Å inward shifts of the Ni atoms towards each other from the sulphur atom plane.

One more point to be mentioned is the absence of short contacts involving C atoms of tert-butyl substituents. It appears that electronic factors are probably responsible for stabilisation of $LM(OOCR)_2$ by CMe_3 groups as substituents.

The Cu···Cu distance in II (2.702 Å) is 0.04 to 0.14 Å longer than in all (rather numerous) Cu(II) carboxylates studied that do not involve too short L···O (carboxylate) contacts (L is an apical ligand) [2]. It also exceeds the Cu···Cu distance in dimeric Cu(II) quinoline-bis-acetate (2.652 Å) [2], but is smaller somewhat than in complexes containing residues of strong carboxylic acids together with α-substituted pyridine ligands. Thus, with L = C_9H_7N and R = $ClCH_2$, FCH_2, and CF_3, the Cu···Cu distance amounts to 2.724, 2.725, and 2.886 Å, respectively, and with L = α-C_6H_7N and R = $ClCH_2$, it is equal to 2.747 Å [2]. According to [2], increase in electron withdrawing power of R results in a small (by some 0.04 Å) increase of the distance between the base planes of Cu coordination polyhedra each containing four carboxylato oxygens.

However, the more important factor is probably strengthening of L–Cu donor–acceptor interactions due to decrease of electron density on Cu. The ensuing shortening of the Cu–N bond should, particularly with bulky axial ligands, enhance interligand repulsions $L\cdots O_{OOCR}$ thus favouring displacement of Cu from the O_4 planes and, accordingly, increasing the Cu···Cu distance. For instance, the decrease of the Cu–N bond length in $[C_9H_7N\cdot Cu(OOCR)_2]_2$ from 2.224 to 2.107 Å on replacing R = CH_3 with CF_3 is accompanied by near as large increase of the distance between the Cu atoms and O_4 planes, from 0.227 to 0.321 Å. As a consequence, the Cu···Cu distance also increases from 2.652 to 2.886 Å [2]. On the other hand, increase in electron density on Cu due to the presence of R = CMe_3 hinders donor–acceptor interactions between copper and acridine which is a weak base. That makes Cu–N bond elongation the more feasible means to eliminate short $C_A\cdots O_{OOCR}$ contacts; in fact, the Cu–N bond length in II increases to 2.371 Å from 2.10–2.20 Å, the usual value for dimeric copper carboxylate adducts [2]. That explains why exceedingly bulky acridine ligands cause only a moderate Cu···Cu distance elongation.

Antiferromagnetic exchange in II containing no direct Cu···Cu bonds (μ_{eff} = 1.22 μ_B (295 K), 0.0 μ_B (79 K); –2J = 340 cm^{-1}) is nearly as strong as in other copper trimethylacetato adducts [11] and stronger than in other copper carboxylates [12]. This observation provides one more proof of exchange over the bond system Cu–O–C–O–Cu being the major exchange mechanism and conforms to the general pattern of strengthening of exchange of this type with electron donor power of R [12].

On the other hand, in the absence of axial ligands hindering approach of copper atoms to each other, direct Cu–Cu bonding with the formation of diamagnetic substances becomes possible, *e.g.* as in dimeric copper bis- diphenyltriazenide, $Cu_2(PhN_3Ph)_4$, where the apical positions are spatially blocked by the phenyl groupings. Like $Ni_2(S_2CCH_2Ph)_4$, this compound does not contain axial ligands; on the other hand, it contains direct Cu–Cu bonds 2.44 Å long [13, 14]. As for tert-butyl substituents, they have no pronounced steric action on the geometry of II as well as I.

The results of the X-ray structure study of I and II thus confirm our earlier suggestions on the important role played by non-bonded interligand interactions in determining structures of binuclear metal carboxylates [15] and the possibility of utilization of these effects in intended syntheses of exchange clusters [4].

At the same time, one should not underestimate the importance of purely electronic effects, such as competition between O_{OOCR} and X_L donor atoms for stronger bonding with the metal, or in other words, for a position in the equatorial plane of a coordination square bipyramid or pyramid. As example, we may point to equatorial binding by copper of such ligands as ammonia, aniline and its derivatives [16–18].

Experimental

The X-ray diffraction data for I were obtained on a Hilger–Watts automatic difractometer using Cu-K_α radiation and following the standard procedure [19]. The crystals are triclynic, $P\bar{1}$, a = 11.168(2), b = 18.334(2), c = 11.452(3) Å, α = 90.37(4), β = 119.01 (1), γ = 89.06(4)°, V = 2050.7(7) Å^3, M = 861, $d_{calc.}$ = 1.40 g/cm^3, Z = 2 (dimer). The intensities of 2282 independent reflections were measured by the ω-scan technique ($\theta \leqslant 57°$), no absorption correction was made. 2091 reflections with $F^2 \geqslant 2\sigma$ were used in structure refinement. The structure was solved by the heavy atom method and refinement to R = 0.091 and R_w = 0.093 by a block-diagonal least squares procedure using anisotropic temperature factors. The unit cell contains two independent dimeric molecules (52 non-hydrogen atoms). Considering the amount of intensity data collected, this explains a not very high accuracy of structure determination.

Anisotropic refinement was carried out using the UMNKSA programme [20]; the Röntgen-70 programme was used in all the other computations [21].

The diffraction data for II were obtained on an automatic difractometer Syntex $P2_1$ using Mo-K_α radiation and following the standard procedure. The crystals are triclynic, $P\bar{1}$, $a = 9.448(4)$, $b = 11.463(5)$, $c = 11.963(4)$ Å; $\alpha = 105.61(3)$, $\beta = 103.40(3)$, $\gamma = 105.91(3)°$; $V = 1132.9(7)$; $M = 444.5$; $d_{\text{calc.}} = 1.31$ g/cm^3, $Z = 1$ (dimer).

The intensities of 3003 independent reflections with $F^2 \geqslant 3\sigma$ were measured by the θ–2θ scan technique. The structure containing 29 independent non-hydrogen atoms was solved as heavy atom problem and refined by block-diagonal least squares treatment to $R = 0.05$ using anisotropic temperature factors. The acridine hydrogen atoms were located from zero synthesis of electron density and fixed in the further refinement. All the computations were made using the standard Syntex programmes for Nova 1200.

Synthesis of $[C_{13}H_9N \cdot Cu(OOCCMe_3)_2]_2$

$[Me_3CCOOH \cdot Cu(OOCCMe_3)_2]_2$ was obtained as recommended in [6] and recrystallized from toluene. A solution of acridine (0.36 g, 2.0 mmol) in 10 ml toluene was added to a green-blue solution of $[Me_3CCOOH \cdot Cu(OOCCMe_3)_2]_2$ (0.74 g, 1.0 mmol) in 10 ml toluene. Green prysms precipitated on concentrating the solution thus obtained. These were recrystallized from toluene, separated from mother liquor, washed with heptane, and dried under vacuum. The yield was 0.62 g (70%). *Anal.*, Found: C, 62.38, H, 6.20; Cu, 13.87%. Calcd. for $C_{46}H_{54}O_8N_2Cu_2$, C, 62.10; H, 6.07; Cu, 14.55%. IR spectrum (KBr disks, ν cm^{-1}): 450 m, 480 m, 535 w, 627 vw, 660 m, 737 vw, 790 s, 855 s, 900 m, 920 s, 960 m, 1020 m, 1235 s, 1380 s, 1430 vs, 1490 vs, 1640 vs, 2890–2990 m, b, 3150 w, b.

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