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Structure of Disodium Nitronitrosylbis[2,4,5,6(1*H*,3*H*)-pyrimidinetetrone 5-oximato(2−)]ruthenate(II) Heptahydrate, $Na_2[Ru(C_4HN_3O_4)_2(NO)(NO_2)].7H_2O$

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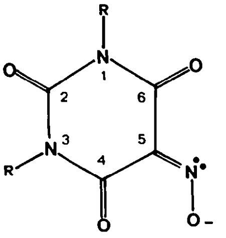
(*Received* 17 *November* 1982; *accepted* 16 *February* 1983)

Abstract. $M_r = 659{\cdot}3$, $P\bar{1}$, $a = 17{\cdot}49$ (1), $b = 9{\cdot}44$ (1), $c = 6{\cdot}74$ (1) Å, $\alpha = 98{\cdot}67$ (5), $\beta = 96{\cdot}02$ (5), $\gamma = 90{\cdot}57$ (5)°, $U = 1094$ (1) Å^3, $Z = 2$, $D_x = 2{\cdot}00$, $D_m = 1{\cdot}96$ (5) Mg m^{-3} (by flotation), Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}86$ mm^{-1}, $F(000) = 660$, room temperature. Full-matrix refinement, 5979 reflections, gave $R = 0{\cdot}033$. The structure consists of Na^+ ions, water molecules and $[Ru(C_4HN_3O_4)_2(NO)(NO_2)]^{2-}$ dianions. The coordination about Ru is octahedral with NO and NO_2 ligands in *cis* arrangement. The Ru—N—O angle is 169·8 (2)°. The chelation of the ketone oximato ligand occurs *via* the atom of the oximato function and the 6-carbonyl function. The mechanism of the nitrosylation reaction is discussed in relationship to the structure of nitrosyl complexes.

Introduction. Ketone oximato ligands are known to stabilize Ru complexes (Brémard, Muller, Nowogrocki & Sueur, 1977). These nitrosyl complexes undergo nucleophilic attack at the nitrosyl group (Brémard, Nowogrocki & Sueur, 1979), as for metal–nitrosyl complexes with a sufficiently high degree of NO^+-like ligand character (Schüg & Guengerich, 1979; Walsh, Bullock & Meyer, 1980; Bottomley, 1978*a*). No X-ray structure of a ketone oximato nitrosyl complex has been reported. In view of the asymmetry of the ketone oximato ligands H_2vi^- and $dmvi^-$ several isomers are possible (Brémard *et al.*, 1977).



$R = H \rightarrow H_2vi^-$: monoanion of 2,4,5,6 (1*H*,3*H*)-pyrimidinetetrone 5-oxime.
$R = CH_3 \rightarrow dmvi^-$: the 1,3-dimethyl derivative.

Knowledge of the unequivocal structure is useful, in particular, for determining the mechanisms of (1), the reversible nitrosylation of $[Ru(H_2vi)_3]^-$ (Brémard *et al.*, 1979) and (2) the nitrosation of organic carbonyls containing an α-methylene group by $Ru(H_2vi)_2(NO)X$ and $Ru(dmvi)_2(NO)X$ (Brémard *et al.*, 1979) (X = Cl, Br, OH). The two series of nitrosyl complexes exhibit two different behaviors towards OH^-: $Ru(dmvi)_2(NO)X$ undergoes the expected nucleophilic attack while $Ru(H_2vi)_2(NO)X$ undergoes deprotonation of the H_2vi^- ligands (Sueur, Brémard & Nowogrocki, 1976). Herein we report the structure determination of $Na_2[Ru(Hvi)_2(NO)(NO_2)].7H_2O$.

Experimental. Solid $Ru(H_2vi)_3NO$, prepared as outlined previously (Brémard *et al.*, 1977), suspended in water (50 ml) was dissolved in NaOH (2×10^{-3}mol) added portionwise to the stirred suspension. A large excess of $NaNO_2$ (5×10^{-2}mol, 3·45 g) was dissolved in the

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solution. The mixture was allowed to stand over one month in darkness at room temperature. Orange single crystals were collected, washed rapidly with ice-cold water and dried over silica-gel. The well formed orange single crystals were suitable for X-ray diffraction study. IR spectra were recorded on a Perkin Elmer 683 spectrometer. The UV–visible spectra were run on a Jobin-Yvon DUOSPAC 203 instrument. Elemental analyses were performed by the Microanalysis Laboratory of the CNRS Villeurbanne, France. {Yield 50%. $\lambda_{\text{max}}(328\text{ nm})$: $\varepsilon = 23\,000$, $\lambda_{sh}(365\text{ nm})$: $\varepsilon = 17\,000\text{ cm}^{-1}\text{ mol}^{-1}$ litre. $\nu(\text{NO}) = 1914$; $\nu(\text{NO}_2) = 1430$, 1240; $\nu(\text{ONO}) = 820\text{ cm}^{-1}$ (KBr); $\nu(\text{NO}) = 1880\text{ cm}^{-1}$ [$(\text{CH}_3)_2\text{SO}$ solution]. Analysis: calculated for $\text{C}_8\text{H}_{16}\text{N}_8\text{Na}_2\text{O}_{18}\text{Ru}$: C 14·57, H 2·43, N 16·99, Na 6·98, Ru 15·33%; found: C 14·6, H 2·5, N 16·7, Na 6·2, Ru 14·4%.}

Intensities of 6886 independent reflections collected for $2 < \theta < 30°$ (index range, $h \pm 24$, $k \pm 13$, l 0–9) on a Philips PW 1100 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation; 5979 classed as observed with $I > 3\sigma(I)$. Cell dimensions determined by least-squares refinement from 2θ, χ, φ angles of 25 reflections. Data corrected for Lorentz and polarization effects, no absorption corrections. A Patterson synthesis could be interpreted in terms of space group $P\bar{1}$ and yielded the position of the Ru atom; refinement and subsequent difference syntheses located the remaining non-hydrogen atoms and revealed seven water O atoms; all atoms in general positions, except Na(2) which occupies the symmetry center at the origin and Na(3) which is randomly distributed over two positions near the center $(0,0,\frac{1}{2})$ with half occupancy. The structure was refined anisotropically by full-matrix least squares (Prewitt, 1966). Final $R = 0·033$ and $R_w = 0·039$; unit weights; scattering factors from Cromer & Waber (1965) for Na^+, Ru^{2+}, C, N, O, H and the anomalous-dispersion corrections from Cromer & Liberman (1970).

Discussion. The final atomic parameters are listed in Table 1.† Interatomic distances and angles are in Table 2.

The characteristic IR absorptions of nitrosyl and nitro groups are observed for $\text{Na}_2[\text{Ru(Hvi)}_2(\text{NO})(\text{NO}_2)]$. The orange nitrosyl complex shows a charge-transfer band at 328 nm ($\varepsilon = 23\,000$); the expected $d\pi \rightarrow \pi^*(\text{NO})$ absorption is probably obscured by broad charge transfer.

The crystal structure consists of $[\text{Ru(Hvi)}_2(\text{NO})(\text{NO}_2)]^{2-}$ anions, Na^+ cations and water molecules (Fig. 1). The coordination polyhedron

Table 1. *Final atomic parameters*

$$B_{\text{eq}} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\text{eq}}(\text{Å}^2)$
Ru	0·76639 (1)	0·53188 (3)	0·66146 (3)	1·496 (5)
O(6)*A*	0·8579 (1)	0·3966 (2)	0·6735 (3)	2·10 (4)
C(6)*A*	0·8950 (1)	0·3901 (3)	0·5165 (4)	1·72 (6)
N(1)*A*	0·9476 (1)	0·2924 (3)	0·4871 (4)	2·18 (6)
C(2)*A*	0·9879 (2)	0·2884 (3)	0·3235 (4)	2·09 (6)
O(2)*A*	1·0343 (1)	0·1948 (2)	0·2821 (4)	3·12 (6)
N(3)*A*	0·9786 (1)	0·3950 (3)	0·2006 (4)	2·28 (6)
C(4)*A*	0·9248 (2)	0·4990 (3)	0·2142 (4)	1·87 (6)
O(4)*A*	0·9202 (1)	0·5886 (2)	0·1000 (3)	2·60 (5)
C(5)*A*	0·8773 (2)	0·4929 (3)	0·3786 (4)	1·75 (6)
N(5)*A*	0·8175 (1)	0·5756 (2)	0·4142 (3)	1·87 (5)
O(5)*A*	0·7948 (1)	0·6678 (3)	0·3071 (4)	3·04 (6)
O(6)*B*	0·7109 (1)	0·3671 (2)	0·4789 (3)	2·10 (4)
C(6)*B*	0·6443 (2)	0·3987 (3)	0·3924 (4)	1·80 (6)
N(1)*B*	0·6038 (1)	0·2980 (3)	0·2689 (4)	2·20 (5)
C(2)*B*	0·5338 (2)	0·3331 (3)	0·1843 (4)	2·21 (6)
O(2)*B*	0·4919 (1)	0·2445 (3)	0·0682 (3)	3·10 (6)
N(3)*B*	0·5064 (1)	0·4714 (3)	0·2280 (4)	2·26 (6)
C(4)*B*	0·5447 (2)	0·5848 (3)	0·3550 (4)	1·97 (6)
O(4)*B*	0·5152 (1)	0·7010 (2)	0·3874 (3)	2·68 (6)
C(5)*B*	0·6195 (2)	0·5438 (3)	0·4430 (4)	1·78 (6)
N(5)*B*	0·6676 (1)	0·6283 (2)	0·5791 (3)	1·85 (6)
O(5)*B*	0·6543 (1)	0·7563 (2)	0·6433 (3)	2·75 (6)
N(6)	0·7167 (1)	0·4594 (3)	0·8993 (4)	2·31 (6)
O(7)	0·6550 (2)	0·5052 (4)	0·9513 (4)	4·59 (9)
O(8)	0·7525 (2)	0·3768 (3)	0·9952 (5)	4·74 (9)
N(7)	0·8021 (1)	0·6898 (3)	0·8161 (4)	2·13 (6)
O(9)	0·8145 (2)	0·7995 (3)	0·9106 (4)	3·66 (7)
Na(1)	0·4116 (1)	0·0717 (1)	0·5334 (2)	2·98 (3)
Na(2)	0·0000	0·0000	0·0000	9·87 (17)
Na(3)	0·0551 (2)	0·9665 (3)	0·4470 (5)	3·77 (8)
W(1)	0·5157 (2)	0·0030 (3)	0·7439 (4)	3·25 (6)
W(2)	0·3447 (2)	0·1733 (3)	0·8231 (4)	3·61 (7)
W(3)	0·2969 (3)	0·9189 (4)	0·9655 (6)	8·24 (16)
W(4)	0·1221 (3)	0·8650 (5)	0·0857 (9)	11·02 (21)
W(5)	0·9530 (3)	0·8894 (4)	0·2489 (5)	8·46 (16)
W(6)	0·3111 (2)	0·9131 (3)	0·3838 (5)	4·59 (8)
W(7)	0·8209 (3)	0·9855 (8)	0·4561 (12)	14·17 (30)

Table 2. *Interatomic distances* (Å) *and angles* (°)

(*a*) Selected distances and angles in the inner coordination sphere of Ru

Ru–O(6)*A*	2·060 (2)	Ru–O(6)*B*	2·005 (6)
Ru–N(5)*A*	2·064 (2)	Ru–N(5)*B*	2·026 (2)
Ru–N(6)	2·099 (3)	Ru–N(7)	1·754 (3)
N(6)–O(7)	1·232 (4)	N(7)–O(9)	1·232 (4)
N(6)–O(8)	1·223 (3)		
O(6)*A*–Ru–N(5)*A*	80·3 (1)	O(6)*B*–Ru–N(5)*B*	80·3 (1)
N(7)–Ru–O(6)*A*	103·3 (2)	N(7)–Ru N(6)	92·1 (2)
N(7)–Ru–N(5)*A*	94·1 (2)	N(7)–Ru N(5)*B*	91·2 (1)
O(6)–Ru–N(6)	94·4 (2)	O(6)*B*–Ru–N(5)*A*	87·4 (1)
N(5)*A*–Ru–N(5)*B*	93·2 (1)	Ru–N(7)- O(9)	169·8 (2)
Ru N(6)–O(7)	121·4 (4)	Ru–N(6)–O(8)	118·7 (4)
O(7)–N(6)–O(8)	119·8 (7)	N(7)–Ru–O(6)*B*	171·4 (2)

(*b*) Interatomic distances and angles in the ligands *A* and *B*

	Ligand *A*	Ligand *B*
C(6)–C(5)	1·456 (4)	1·443 (4)
C(5)–C(4)	1·460 (5)	1·460 (5)
C(4)–O(4)	1·224 (4)	1·217 (4)
C(4)–N(3)	1·366 (4)	1·384 (4)
N(3)–C(2)	1·397 (4)	1·395 (4)
C(2)–O(2)	1·227 (4)	1·233 (4)
C(2)–N(1)	1·366 (4)	1·361 (4)
N(1)–C(6)	1·318 (3)	1·313 (4)
C(6)–O(6)	1·292 (3)	1·305 (4)
C(5) N(5)	1·332 (4)	1·338 (3)
N(5)–O(5)	1·254 (4)	1·253 (3)
N(1)–C(6)–C(5)	122·3 (5)	124·2 (5)
C(6)–C(5)–C(4)	119·2 (5)	119·5 (5)
C(5)–C(4)–N(3)	113·3 (5)	111·9 (4)
C(4)–N(3)–C(2)	125·4 (6)	125·9 (5)
N(3)–C(2)–N(1)	120·2 (5)	120·9 (5)
C(2)–N(1)–C(6)	119·1 (5)	117·6 (5)
O(2)–C(2)–N(3)	117·9 (5)	117·4 (5)
C(5)–C(4)–O(4)	125·3 (6)	127·0 (6)
O(6)–C(6)–C(5)	118·3 (5)	116·9 (5)
C(6)–C(5) N(5)	116·0 (4)	114·9 (4)
C(5)–N(5)–O(5)	123·3 (6)	123·4 (4)

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† Lists of structure factors, anisotropic thermal parameters, mean-plane calculations, and intermolecular contacts have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38439 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

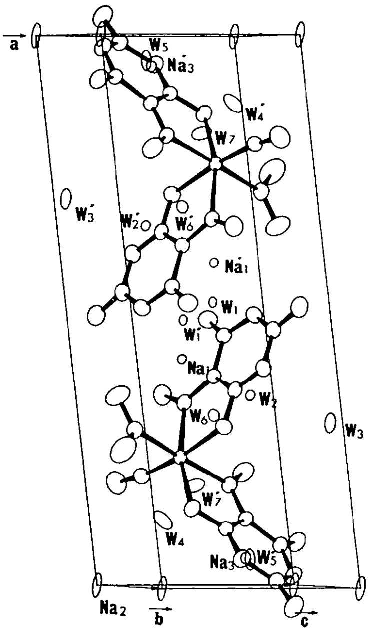

Fig. 1. The packing in the title compound.

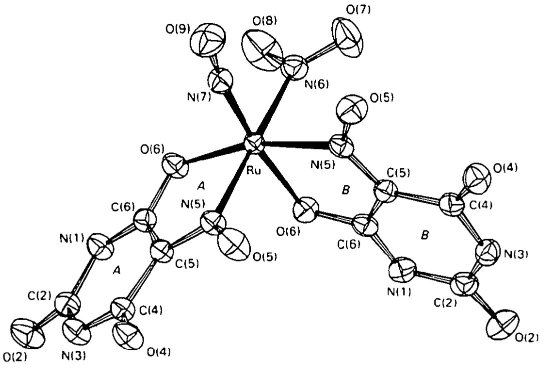

Fig. 2. View of the $[Ru(Hvi)_2(NO)(NO_2)]^{2-}$ dianion showing the atom-labeling scheme. The two H atoms are omitted. 50% probability ellipsoids are shown.

around Na^+ comprises six atoms forming a deformed octahedron: four O(*W*) atoms and two O or N atoms belonging to Hvi or NO_2 ligands. The water molecules are H-bonded to free ends of NO_2 or carbonyl or nitrosyl functions. The H bonds contribute to the stabilization of the crystal packing. The inner coordination geometry of $[Ru(Hvi)_2(NO)(NO_2)]^{2-}$ is shown in Fig. 2. Ru is six-coordinated with the NO and NO_2 groups occupying adjacent coordination sites. The chelate bite of the Hvi ligands, 80·3 (1)°, is analogous to those reported for the trischelate in $H[Ru(H_2vi)_3].4H_2O$ (Abraham, Nowogrocki, Sueur & Brémard, 1978) and induces distortion from ideal octahedral geometry. The distortion is reflected in inter- and intraligand bond angles, and in the dihedral angles between mean planes defined by Ru, O(6)*A*, C(6)*A*, C(5)*A*, N(5)*A*, by Ru, O(6)*B*, C(6)*B*, C(5)*B*, N(5)*B* and by Ru, N(6), N(7) which range from 74·26 (8) to 87·8 (1)°. The atoms of Hvi ligands *A* and *B* are coplanar. Although the H atoms of the pyrimidine rings were not unequivocally located, a final difference Fourier map shows significant peaks at 1 Å from the N(3) sites of the pyrimidine rings; no peak is detected in the vicinity of the N(1) sites. These features are in good accord with deprotonation of the N(1) sites. The deviations of the interatomic distances and angles in the Hvi*A* and Hvi*B* ligands from those of H_2vi in $[Ru(H_2vi)]^-$ (Abraham *et al.*, 1978) are significant in several cases. The four atoms of the Ru—NO_2 moiety are coplanar, but the NO_2 group is slightly twisted [6·5 (3)°] out of the plane defined by O(6)*A*, N(5)*A*, N(5)*B* and N(6). The distances and angles of the NO_2 group are in the expected range for nitro complexes (Ileperuma & Feltham, 1977; Bottomley, 1978*b*).

The relative size, shape and orientation of the thermal ellipsoids of N(7) and O(9) (Fig. 2) show that the atoms are not disordered and that the thermal motion is physically reasonable; B_{eq} values are 2·13 and 3·66 Å^2 for N(7) and O(9), respectively. The deviation of Ru—N—O from linearity [169·8 (2)°] is thus real and not an artefact. Deviations from linearity up to 15° have been ascribed to crystal-packing forces and/or unsymmetrical π bonding of the metal to the NO ligand (Bottomley, 1978*b*; Hoffmann, Chen & Thorn, 1977). O(6)*B* of the Hvi*B* ligand lies in the plane of Ru, N(7) and O(9), the angle defined by N(7)—Ru—O(6)*B* is 171·4 (2)° and O(9) of the nitrosyl group is bent towards O(5)*B* of the oximato function of the Hvi*B* ligand. The absence of lengthening of the Ru—O(6) bond *trans* to the N(7)—O(9) group is consistent with the lack of strong structural *trans* effects in metal nitrosyls with linear *M*—N—O groups (Bottomley, 1978*b*). From previous investigations of the *trans* influence of the nitrosyl ligand in metal nitrosyls $\{M\text{NO}\}^6$, it was found that NO is a poor σ-bonding ligand, but a good π acceptor. A *trans* atom such as O(6)*B* is able to act as a good σ donor and induces a slight shortening of the *trans* Ru—O(6)*B* bond [2·005 (2) Å] compared to the *cis* Ru—O(6)*A* bond [2·060 (2) Å]. The Ru—N(5)*A* bond is 0·04 Å longer than the Ru—N(5)*B* bond and may reflect a structural *trans* effect of the NO_2 group (Ileperuma & Feltham, 1977).

The deprotonation of the H_2vi ligands of $Ru(H_2vi)_2NO(NO_2)$ at the N(1) sites induces shifts of the characteristic vibration frequencies ν(C—O), ν(C=N) and ν(NO). The bathochromic shift of ν(NO) from 1950 cm^{-1} for $[Ru(H_2vi)_2(NO)(NO_2)]$ to 1914 cm^{-1} for $[Ru(Hvi)_2(NO)(NO_2)]^{2-}$ upon deprotonation is evidence for the increase of the back-donation $d\pi\rightarrow\pi^*$ for NO and demonstrates the synergistic bonding effect of NO and H_2vi ligands through the Ru atom.

The spectroscopic (Brémard *et al.*, 1977; Sueur *et al.*, 1976) and X-ray data show that it is reasonable to assume the same molecular arrangement for neutral and anionic nitrosyl complexes. The stereochemistry of the reversible nitrosylation of *fac*-$[Ru(H_2vi)_3]^-$ by nitrous acid (Brémard, Nowogrocki & Sueur, 1978) can be verified by the knowledge of the molecular structure of $[Ru(Hvi)_2(NO)(NO_2)]^{2-}$. The rate-determining step of the nitrosylation reaction is the breaking of the chelate ring at the Ru—N(5) bond. The lower-coordinated polyhedron has a very short lifetime and an octahedral complex is reformed by bond formation at Ru—N(5) to give the starting *fac*-$[Ru(H_2vi)_3]^-$ or by NO^+ addition to give *cis*-$Ru(H_2vi)_3NO$ with a dangling (unidentate) H_2vi^- ligand. *cis*-$Ru(H_2vi)_3NO$ then reacts with NO_2^- by rupture of the Ru—O(6) bond of the unidentate H_2vi ligand to give a *cis cis cis* octahedral complex, $Ru(H_2vi)_2(NO)(NO_2)$. The most striking feature of the mechanism is the reversible chelate-ring opening by breaking of the Ru—N(5) bond (1·95 Å) in *fac*-$[Ru(H_2vi)_3]^-$ whereas Ru—O(6) (2·11 Å) is longer than Ru—N(5) (Abraham *et al.*, 1978). The overall dissociation of *fac*-$[Ru(H_2vi)_3]^-$ occurs by acid catalysis of the bond rupture with protonation of the O(5) site of the oxime function. The proposed mechanism of the overall nitrosylation is checked by the solvolysis of *cis*-$Ru(H_2vi)_3NO$ (Brémard *et al.*, 1978). The geometries of the isolated complexes *fac*-$[Ru(H_2vi)_3]^-$ (Abraham *et al.*, 1978) and $Na_2[Ru(Hvi)_2(NO)(NO_2)]$ (this work) are in good accord with retention of configuration in nitrosylation reactions.

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Bis{μ-chloro-[*N*,*N'*-ethanediylidenebis(1-isopropyl-2-methylpropylamine)]copper(I)}, $[Cu_2(C_{16}H_{32}N_2)_2Cl_2]$

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(*Received* 18 *October* 1982; *accepted* 15 *March* 1983)

Abstract. $M_r = 702{\cdot}88$, tetragonal, $I4_1/a$, $a = b = 25{\cdot}416\ (33)$, $c = 12{\cdot}524\ (11)$ Å, $V = 8090\ (2)$ Å^3, $Z = 8$, $D_x = 1{\cdot}154\ (3)$ g cm^{-3}, $D_m = 1{\cdot}16$ g cm^{-3}, Mo $K\alpha$: $\lambda = 0{\cdot}70926$ Å, $\mu = 11{\cdot}5$ cm^{-1}, $T = 298$ K, $F(000) = 3008$, $R = 0{\cdot}063$ for 1610 reflections. The title compound is an unsymmetrically chloro-bridged dimer; the copper coordination is in agreement with the observed dissociation in solution.

Introduction. Recently, Kitagawa & Munakata (1981) reported on the reaction of carbon monoxide with (bipyridyl)chlorocopper(I), for which they proposed a dimeric chloro-bridged structure based on UV intensity arguments. Although such a structure does not seem unlikely, we have found that slight changes in the steric environment of comparable ligands of the 1,4-diaza-1,3-diene (dad) type (1) have substantial influence on the copper(I) complexes formed. Reaction of dad with copper(I) halides in a 1:1 ratio gives strongly coloured complexes of composition (dad)Cu*X* (2) for which we claimed (tom Dieck & Renk, 1971) a three-coordinate trigonal structure, while Ayranci, Daul, Zobrist & von Zelewsky (1975) ascribed to them the preponderant structure $[(dad)_2Cu]^+[CuX_2]^-$ (2*a*: *R* = *tert*-butyl), being subject to further solution equilibria.

0108-2701/83/070841-03$01.50