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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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)CuX (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.

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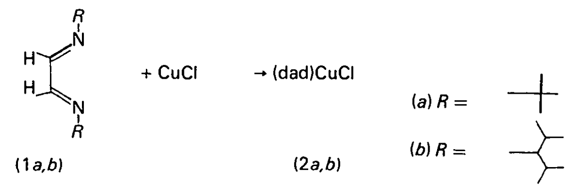

We have now synthesized complex (2*b*) which shows a unique behaviour and settles the question of coordination number *vs* colour. Crystals of (2*b*) are dark red [wavelength of maximum absorption in the solid state λ_m (solid) 510 nm] similar to the solution and solid-state colour of (2*a*), but in solvents of all kinds of polarity a light greenish colour [λ_m (solut.) 365–383 nm] appears. The red colour is restored on evaporation even when very dilute solutions are left to dry on filter paper. Especially because of this property a structural investigation of (2*b*) seemed promising.

Experimental. Slow evaporation after filtration of a solution (stirred for 2 h) of CuCl and (1*b*) in ethanol at room temperature. Size of sample: 0·2 × 0·15 × 0·35 mm. 2253 independent, not systematically absent (in $I4_1/a$) reflections measured in the $\theta/2\theta$ scan mode out to $2\theta = 42{\cdot}5°$ on a Syntex $P2_1$ diffractometer; $h/k/l$ range: 25/25/12. Cell parameters obtained by least-squares refinement from setting angles of 13 automatically centred reflections on the diffractometer. Standard reflections $6\bar{7}1$, $\bar{1}23$; no intensity decrease during measurement. No absorption or secondary-extinction corrections applied. Structure solved by Patterson and Fourier methods [*MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); *SHELX*77 (Sheldrick, 1977)]. After refining all non-hydrogen atoms with anisotropic temperature factors [$\sum w(\Delta F^2)^2$ minimized] the positions of all H atoms were calculated geometrically; in the following refinement cycles they were allowed to ride on their corresponding C atoms, except for the methyl groups which were refined as rigid groups. Final conventional R factor 0·063 for 1610 structure factors with $|F| > 3\sigma(|F|)$; $Rw = \sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2 = 0{\cdot}044$, $w = 2{\cdot}1316/\sigma^2(|F|)$. The final difference map showed no peak > 0·3 e Å^{-3}; all shift/error values < 0·08. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Plots performed with program *SCHAKAL* (E. Keller, Univ. Freiburg, unpublished).

Table 1. *Atomic parameters*

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq}(Å^2)
Cu	0·4528 (1)	0·2858 (1)	0·6239 (1)	0·061 (1)
Cl	0·4566 (1)	0·1982 (1)	0·6605 (1)	0·052 (1)
N(1)	0·4044 (2)	0·3244 (2)	0·5163 (5)	0·049 (5)
N(2)	0·4234 (2)	0·3466 (2)	0·7277 (5)	0·055 (5)
C(1)	0·3874 (3)	0·3665 (3)	0·5588 (8)	0·072 (7)
C(2)	0·3985 (4)	0·3794 (3)	0·6692 (8)	0·074 (7)
C(10)	0·3900 (3)	0·3138 (3)	0·4033 (6)	0·052 (6)
C(11)	0·4396 (3)	0·3022 (3)	0·3425 (6)	0·064 (6)
C(12)	0·3464 (3)	0·2723 (3)	0·3957 (6)	0·058 (6)
C(20)	0·4324 (3)	0·3608 (3)	0·8393 (7)	0·062 (7)
C(21)	0·4911 (3)	0·3603 (3)	0·8659 (7)	0·070 (7)
C(22)	0·3981 (3)	0·3250 (4)	0·9148 (6)	0·075 (7)
C(111)	0·4776 (3)	0·3489 (3)	0·3428 (7)	0·093 (8)
C(112)	0·4274 (3)	0·2849 (4)	0·2255 (7)	0·092 (9)
C(121)	0·2992 (3)	0·2884 (3)	0·4647 (7)	0·089 (7)
C(122)	0·3655 (3)	0·2165 (3)	0·4315 (6)	0·076 (7)
C(211)	0·5193 (3)	0·4019 (4)	0·7972 (7)	0·098 (8)
C(212)	0·5023 (4)	0·3698 (4)	0·9841 (7)	0·107 (10
C(221)	0·3396 (3)	0·3287 (4)	0·8830 (8)	0·122 (10)
C(222)	0·4156 (3)	0·2672 (4)	0·9161 (6)	0·084 (7)

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s*

Cu—Cl	2·276 (2)	Cu—Cu′	3·011 (2)
Cu—Cl′	2·378 (2)	Cl—Cl′	3·549 (2)
Cu—N(1)	2·071 (6)	Cu—N(2)	2·154 (6)
N(1)—C(1)	1·272 (11)	N(2)—C(2)	1·276 (11)
C(1)—C(2)	1·450 (13)		
N(1)—C(10)	1·486 (10)	N(2)—C(20)	1·461 (11)
C(10)—C(11)	1·503 (10)	C(20)—C(21)	1·528 (11)
C(10)—C(12)	1·532 (10)	C(20)—C(22)	1·576 (12)
C(11)—C(111)	1·530 (11)	C(21)—C(211)	1·540 (12)
C(11)—C(112)	1·560 (12)	C(21)—C(212)	1·527 (13)
C(12)—C(121)	1·534 (11)	C(22)—C(221)	1·543 (12)
C(12)—C(122)	1·563 (11)	C(22)—C(222)	1·533 (13)
Cl—Cu—Cl′	99·4 (2)	Cu—Cl—Cu′	80·6 (2)
N(1)—Cu—Cl	128·2 (2)	N(1)—Cu—Cl′	112·1 (2)
N(2)—Cu—Cl	126·5 (2)	N(2)—Cu—Cl′	108·9 (2)
N(1)—Cu—N(2)	81·2 (2)		
C(1)—N(1)—Cu	109·2 (5)	C(2)—N(2)—Cu	107·1 (6)
C(1)—C(2)—N(2)	119·8 (7)	C(2)—C(1)—N(1)	121·5 (8)
C(1)—N(1)—C(10)	117·8 (6)	C(2)—N(2)—C(20)	117·7 (6)
C(11)—C(10)—N(1)	108·2 (6)	C(21)—C(20)—N(2)	111·1 (7)
C(12)—C(10)—N(1)	111·1 (6)	C(22)—C(20)—N(2)	110·1 (6)
C(12)—C(10)—C(11)	116·1 (6)	C(22)—C(20)—C(21)	113·7 (7)
C(111)—C(11)—C(10)	112·1 (6)	C(211)—C(21)—C(20)	109·0 (7)
C(112)—C(11)—C(10)	111·4 (6)	C(212)—C(21)—C(20)	113·2 (7)
C(212)—C(21)—C(211)	110·2 (7)	C(212)—C(21)—C(211)	110·2 (7)
C(121)—C(12)—C(10)	110·3 (6)	C(221)—C(22)—C(20)	110·0 (7)
C(122)—C(12)—C(10)	112·6 (6)	C(222)—C(22)—C(20)	113·6 (7)
C(122)—C(12)—C(121)	108·8 (6)	C(222)—C(22)—C(211)	110·0 (7)

Discussion. Table 1 gives the atomic parameters,* Table 2 the bond distances and corresponding angles. The molecular structure (Fig. 1) shows a chloro-bridged dimer of formula unit (dad)Cu*X* (eight dimers in the unit cell). The environment of each copper(I) is distorted tetrahedral. The angle N(1)—Cu—N(2) is determined by the bite of the chelate ligand and is comparable to other structures of (1) with first-row transition elements (Svoboda, tom Dieck, Krüger & Zsay, 1981; tom Dieck, Svoboda & Greiser, 1981; tom Dieck, Svoboda & Kopf, 1978) The most important deviation from a 'regular' environment of copper in a $[CuA_2B_2]$ complex is the unsymmetrical bridging position of each chloro ligand relative to copper. The

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38436 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

two Cu—Cl distances show a difference of 0·1 Å; even more pronounced is the difference between the angles $(N_1/N_2)^*$—Cu—Cl (143·0°) *vs* $(N_1/N_2)^*$—Cu—Cl′ (117·6°).

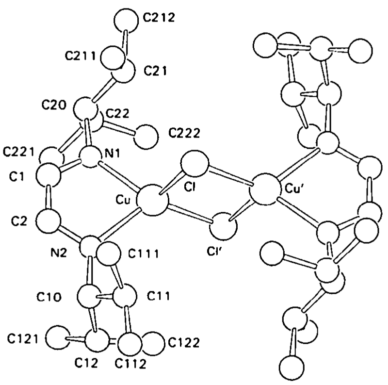

Fig. 1. *SCHAKAL* plot and numbering scheme of (2*b*).

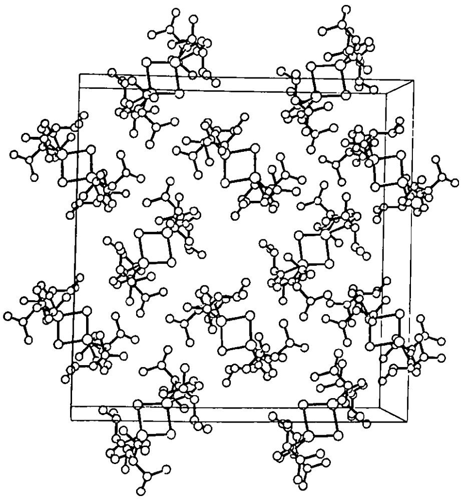

Fig. 2. View of the unit cell along the *c* axis.

The observed structure (Fig. 2) is in agreement with the observed dissociation of (2*b*) in solution into two three-coordinate species (dad)CuCl. Solid (2*b*) is a red crystalline material with $\lambda_m = 510$ nm, while in all solvents $\lambda_m \simeq 375$ nm. The molecular weight in dichloromethane or acetone was determined as 360 ± 20 (calculated for the monomer: 351·4); the solution in acetone showed no conductivity. The steric requirements of the *N*-alkyl substituent in (2*b*) are obviously responsible for the reduced interaction between two such species also in the solid state and (1*b*) avoids completely the complex type $[(dad)_2Cu]^+[CuCl_2]^-$ encountered for (2*a*) (*R* = *tert*-butyl). The half width of the solid state CT band (metal-to-ligand type charge-transfer transition) of (2*b*) (5500 cm^{-1}) is, in agreement with this structure, about 50% greater than for (2*a*) (3500 cm^{-1}).

We thank Dr J. Kopf and Mr D. Melzer for valuable discussion in the course of the structural work.

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* (N_1/N_2) means the intersection of the line through N(1),N(2) and the plane through Cu, Cl, Cl′.

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Structure of μ-Oxo-(pyrimidine)-μ-sulphido-bis{[(*O*,*O*′-diisopropylphosphorodithioato)-*S*,*S*′]oxomolybdenum(V)}, $Mo_2(C_4H_4N_2)(C_6H_{14}O_2PS_2)_2O_3S$

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Abstract. $M_r = 778\cdot4$, Aa, $a = 11\cdot854$ (8), $b = 9\cdot000$ (7), $c = 28\cdot849$ (13) Å, $\beta = 93\cdot27$ (6)°, $U = 3072\cdot7$ Å^3, $Z = 4$, $D_m = 1\cdot67$ (1), $D_x = 1\cdot68$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot7107$ Å, $\mu = 12\cdot51$ cm^{-1}, $F(000) = 1568$, $T = 298$ K, $R = 0\cdot065$ for 2250 independent reflections. This molecule (II) is the 1:1 adduct of

0108-2701/83/070843-03$01.50