Table 2. *Bond distances* (Å) *and bond angles* (°)

Cu1–O1	1·914 (2)	Cu2–N1′	1·988 (3)
Cu1–O1	1·919 (2)	Cu2–N2′	1·994 (3)
Cu1–O2	2·681 (4)	Cu3–Cl1	2·252 (1)
Cu1–N1	1·979 (3)	Cu3–Cl2	2·242 (1)
Cu1–N2	1·984 (3)	Cu3–Cl3	2·279 (1)
Cu2–O1′	1·908 (2)	Cu3–Cl4	2·228 (1)
Cu2–O1′	1·900 (3)		
O1–Cu1–O1	76·7 (1)	O1′–Cu2–N1′	165·9 (1)
O1–Cu1–O2	83·4 (1)	O1′–Cu2–N2′	92·6 (1)
O1–Cu1–N1	168·5 (1)	O1′–Cu2–N1′	91·8 (1)
O1–Cu1–N2	92·7 (1)	O1′–Cu2–N2′	169·2 (1)
O1–Cu1–O2	95·0 (1)	N1′–Cu2–N2′	99·0 (1)
O1–Cu1–N1	92·3 (1)	Cl1–Cu3–Cl2	97·64 (5)
O1–Cu1–N2	169·2 (1)	Cl1–Cu3–Cl3	132·43 (5)
O2–Cu1–N1	101·1 (1)	Cl1–Cu3–Cl4	100·05 (5)
O2–Cu1–N2	81·7 (1)	Cl2–Cu3–Cl3	98·77 (5)
N1–Cu1–N2	98·4 (1)	Cl2–Cu3–Cl4	134·00 (6)
O1′–Cu2–O1′	76·7 (1)	Cl3–Cu3–Cl4	99·78 (5)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Cs_2CuCl_4 (Morosin & Lingafelter, 1961), Cl—Cu—Cl range from 102·5 to 124·9°, and the planar conformation in the 2-aminobenzothiazolium salt (Antolini, Benedetti, Fabretti & Giusti, 1988). A nearly identical 'flattening' angle (Smith, 1976) was recently reported (Koman, Siroklin, Andrejovic, Corradi & Battaglia, 1988) for $[iso\text{-}Bu_2NH_2]_2[CuCl_4]$ where the Cl—Cu—Cl angles range from 97·2–138·6°, and the average Cu—Cl distance of 2·249 (7) Å is identical with the present value of 2·250 (15) Å. Longer distances are associated with greater flattening (Smith, 1976). There is also considerable variation in the Cu3—Cl distances [2·228 (1) to 2·279 (1) Å]. This variation can be correlated with the extent of the interaction of the chloride ligands with the Cu^{II} atoms in the binuclear complexes (see above) and with the water molecule through hydrogen bonding (see below).

Other than the chloride bridges between copper ions, there are no unusually short intramolecular contacts. Water hydrogens are involved in relatively weak hydrogen bonds with Cl2 and Cl3 of the $[CuCl_4]^{2-}$ ion [O2···Cl3, 3·308 (1) Å; O2—H1O2···Cl3, 143°; O2···Cl2, 3·250 (1) Å; O2—H2O2···Cl2, 122°] (see Fig. 3).

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Structure of a Dipotassium Tetrathiocyanatomercurate(II) Salt with Dibenzo-18-crown-6

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Abstract. Bis[(dibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadeca-2,11-diene)potassium] tetrathiocyanatomercurate(II) ethanolate, $[K(C_{20}H_{24}O_6)]_2[Hg(SCN)_4].C_2H_5OH$, $M_r = 1278{\cdot}0$, monoclinic, $C2/c$, $a = 29{\cdot}763\ (5)$, $b = 14{\cdot}690\ (3)$, $c = 25{\cdot}314\ (5)$ Å, $\beta = 99{\cdot}06\ (1)°$, $U = 10930\ (3)$ Å^3, $Z = 8$, $D_m = 1{\cdot}55\ (3)$, $D_x = 1{\cdot}55$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 31{\cdot}69$ cm^{-1}, $F(000) = 5095$, at 153 K, final $R = 0{\cdot}042$ for 4599 $[I > 3\sigma(I)]$ independent observed reflections. The molecule consists of two dibenzo-18-crown-6 potassium cations linked through three out of the four end N atoms of the tetrathiocyanatomercurate(II) anion. In addition to the six O atoms in the crown ether one potassium is coordinated to a thiocyanate N atom with K···N distance of 2·727 (11) Å, while the other potassium is coordinated to two other N atoms with K···N distances 2·961 (11) and 2·924 (11) Å respectively. The longer distances observed in the latter case

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are a consequence of accommodating two coordinating groups on the same side of the O_6 plane. The solvent molecule is partially disordered.

Introduction. It is well known that dibenzo-18-crown-6 forms very stable complexes with simple potassium salts (Dobler, 1981; Izatt, Eatough, & Christensen, 1973) and the structure of some of these has been reported (Aldoshin, D'yachenko, Tkachev & Atovmyan, 1981; Hilgenfeld & Saenger, 1981). Although this crown ether also complexes with simple mercury(II) salts (Kawasaki & Matsuura, 1984) its complex formation with potassium mercurate(II) salts is relatively unknown with the exception of the tetrathiocyanate complex reportedly identified by its infrared spectrum (Poladyan, Ermakov, Sokolova, Avlesovich, Pakhol'chuk & Mukelo, 1984) and the structure of the tetracyanide complex (Mok, McKee & Robinson, 1987). We report here the structure of the dibenzo-18-crown-6 complex with dipotassium tetrathiocyanatomercurate(II).

Experimental. Compound prepared by reacting an aqueous ethanol solution of dipotassium tetrathiocyanatomercurate(II) with a chloroform solution of dibenzo-18-crown-6. Elemental analysis indicated formula of $[K(C_{20}H_{24}O_6)]_2[Hg(SCN)_4].C_2H_5OH$ (Mok, 1988). Density by flotation in CCl_4/petroleum ether. Crystal size approximately $0{\cdot}2 \times 0{\cdot}3 \times 0{\cdot}6$ mm. Nicolet *R3m* four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation, using Nicolet low temperature device. Cell dimensions derived by least-squares calculations from angular settings of 23 reflections measured at $23 < 2\theta < 35°$, ω scan mode at $6{\cdot}51°\ \text{min}^{-1}$ scan rate. Three standards measured every 97 reflections: no significant variations in intensity. 7594 reflections measured, $2\theta_{\max} = 45°$, $0 \leq h \leq 33$, $0 \leq k \leq 16$, $-28 \leq l \leq 28$. Data reduction gave 7117 unique reflections. Statistical analysis of data suggested space group $C2/c$. Numerical absorption correction applied using face indexing, *SHELXTL*, revision 4·1 (Sheldrick, 1984), max. and min. transmission factors 0·37, 0·25. Hg atom located by Patterson methods and other non-H atoms from difference Fourier maps. 4599 data with $I > 3\sigma(I)$ used in subsequent calculations. All non-H atoms except those in solvent molecule and C(49) refined anisotropically; solvent atoms located after refinement on F to below 0·06. H atoms placed at fixed distance (0·96 Å) from C or O atoms; their thermal parameters were given 1·2 times the isotropic values of their carrier atoms and were not refined. Weighting scheme $w = [\sigma^2(F) + 0{\cdot}0009F^2]^{-1}$. Final $R = 0{\cdot}042$, $wR = 0{\cdot}057$, $S = 1{\cdot}394$ with final max. shift/e.s.d. < 0·03. In final difference map maximum and minimum heights +1·8 and −0·5 e Å^{-3}; location of high peaks in difference map in vicinity of Hg atom or solvent molecule. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations initially performed on Nova 4X computer, final calculations on Data General 30 computer using *SHELXTL*, revision 5·1 (Sheldrick, 1985).

Table 1. *Atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* (Å$^2 \times 10^3$)

	x	*y*	*z*	*U*
Hg	1754·2 (1)	6688·1 (3)	7401·3 (2)	37 (1)*
S(1)	2031 (1)	5205 (2)	7812 (1)	50 (1)*
C(1)	2577 (4)	5452 (7)	7998 (4)	33 (4)*
N(1)	2958 (4)	5607 (7)	8137 (4)	48 (4)*
S(2)	1121 (1)	6436 (2)	6587 (1)	39 (1)*
C(2)	1475 (4)	6013 (7)	6195 (4)	35 (4)*
N(2)	1714 (3)	5709 (6)	5919 (4)	52 (4)*
S(3)	2211 (1)	7841 (2)	6989 (1)	42 (1)*
C(3)	2727 (4)	7546 (7)	7271 (5)	41 (5)*
N(3)	3096 (4)	7356 (8)	7471 (5)	69 (5)*
S(4)	1296 (1)	7398 (2)	8083 (1)	45 (1)*
C(4)	988 (4)	6441 (9)	8121 (4)	56 (5)*
N(4)	788 (4)	5755 (8)	8141 (5)	78 (5)*
K(1)	3840 (1)	6573 (2)	8227 (1)	33 (1)*
O(11)	4096 (2)	8400 (5)	8264 (3)	38 (3)*
C(12)	3951 (4)	8774 (7)	7740 (4)	41 (4)*
C(13)	4248 (4)	8380 (7)	7373 (4)	42 (4)*
O(14)	4203 (2)	7412 (4)	7362 (3)	32 (3)*
C(15)	4465 (3)	6965.(6)	7045 (4)	25 (3)*
C(16)	4731 (4)	7383 (7)	6724 (4)	34 (4)*
C(17)	4978 (3)	6857 (8)	6417 (4)	44 (5)*
C(18)	4953 (4)	5941 (9)	6415 (4)	41 (4)*
C(19)	4687 (4)	5511 (8)	6744 (4)	39 (4)*
C(20)	4440 (3)	6020 (7)	7061 (4)	26 (3)*
O(21)	4164 (2)	5643 (4)	7398 (3)	30 (2)*
C(22)	4198 (4)	4660 (7)	7458 (4)	37 (4)*
C(23)	3905 (4)	4381 (7)	7867 (4)	37 (4)*
O(24)	4095 (2)	4740 (4)	8372 (2)	30 (2)*
C(25)	3859 (4)	4420 (7)	8788 (4)	36 (4)*
C(26)	4109 (4)	4779 (6)	9312 (4)	34 (4)*
O(27)	4094 (2)	5752 (4)	9288 (3)	31 (3)*
C(28)	4286 (4)	6216 (7)	9739 (4)	34 (4)*
C(29)	4496 (4)	5789 (8)	10210 (4)	41 (4)*
C(30)	4686 (4)	6343 (9)	10637 (5)	54 (5)*
C(31)	4665 (4)	7278 (9)	10606 (5)	55 (5)*
C(32)	4466 (4)	7660 (8)	10136 (4)	42 (4)*
C(33)	4278 (4)	7162 (7)	9705 (4)	34 (4)*
O(34)	4062 (2)	7505 (4)	9224 (3)	34 (3)*
C(35)	4044 (4)	8467 (7)	9186 (4)	42 (4)*
C(36)	3815 (4)	8719 (7)	8638 (5)	48 (5)*
K(2)	2360 (1)	4961 (2)	5398 (1)	31 (1)*
O(41)	2861 (2)	4527 (5)	6380 (3)	33 (3)*
C(42)	2943 (4)	5400 (7)	6631 (4)	40 (4)*
C(43)	3302 (4)	5856 (8)	6359 (4)	40 (4)*
O(44)	3088 (2)	6059 (5)	5815 (2)	32 (2)*
C(45)	3354 (3)	6462 (6)	5495 (4)	24 (3)*
C(46)	3801 (4)	6698 (7)	5632 (4)	34 (4)*
C(47)	4037 (4)	7146 (7)	5278 (4)	36 (4)*
C(48)	3817 (4)	7357 (6)	4760 (4)	30 (4)*
C(49)	3363 (3)	7125 (7)	4615 (4)	29 (2)
C(50)	3130 (3)	6695 (7)	4969 (4)	26 (3)*
O(51)	2682 (2)	6427 (4)	4861 (2)	28 (2)*
C(52)	2453 (3)	6584 (7)	4319 (4)	34 (4)*
C(53)	1975 (4)	6248 (7)	4284 (4)	36 (4)*
O(54)	1981 (2)	5287 (4)	4352 (3)	31 (2)*
C(55)	1532 (3)	4923 (7)	4314 (4)	33 (4)*
C(56)	1579 (4)	3910 (7)	4350 (4)	33 (4)*
O(57)	1789 (2)	3666 (5)	4877 (3)	33 (3)*
C(58)	1845 (3)	2750 (7)	4999 (4)	28 (4)*
C(59)	1687 (4)	2074 (7)	4659 (4)	36 (4)*
C(60)	1731 (4)	1177 (7)	4822 (5)	40 (5)*
C(61)	1954 (4)	969 (8)	5334 (5)	52 (5)*
C(62)	2131 (4)	1668 (7)	5677 (4)	38 (4)*
C(63)	2066 (4)	2540 (7)	5507 (4)	29 (4)*
O(64)	2208 (2)	3288 (5)	5826 (3)	36 (2)*
C(65)	2467 (4)	3091 (7)	6350 (4)	35 (4)*
C(66)	2549 (4)	4002 (8)	6640 (4)	42 (4)*
O(70)	289 (5)	5465 (10)	5253 (6)	50 (4)
C(71)	343 (8)	5446 (17)	4789 (10)	55 (7)
C(72)	141 (9)	5042 (19)	4303 (10)	61 (7)
O(80)	142 (7)	1845 (13)	3027 (7)	77 (6)
C(81)	−83 (6)	2527 (12)	2774 (7)	106 (6)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Selected bond lengths* (Å) *and bond angles* (°)

Hg—S(1)	2·497 (3)	Hg—S(2)	2·591 (3)
Hg—S(3)	2·499 (3)	Hg—S(4)	2·582 (3)
S(1)—C(1)	1·659 (12)	C(1)—N(1)	1·155 (15)
N(1)—K(1)	2·961 (11)	S(2)—C(2)	1·677 (12)
C(2)—N(2)	1·162 (15)	N(2)—K(2)	2·727 (11)
S(3)—C(3)	1·647 (13)	C(3)—N(3)	1·169 (17)
N(3)—K(1)	2·924 (11)	S(4)—C(4)	1·689 (13)
C(4)—N(4)	1·175 (18)	K(1)—O(11)	2·789 (7)
K(1)—O(14)	2·868 (7)	K(1)—O(21)	2·800 (7)
K(1)—O(24)	2·806 (7)	K(1)—O(27)	2·932 (7)
K(1)—O(34)	2·855 (7)	K(2)—O(41)	2·764 (6)
K(2)—O(44)	2·773 (7)	K(2)—O(51)	2·796 (7)
K(2)—O(54)	2·752 (6)	K(2)—O(57)	2·746 (7)
K(2)—O(64)	2·751 (7)		
S(1)—C(1)—N(1)	178·3 (10)	C(1)—N(1)—K(1)	159·0 (8)
S(2)—C(2)—N(2)	178·8 (8)	C(2)—N(2)—K(2)	172·0 (8)
S(3)—C(3)—N(3)	178·5 (11)	C(3)—N(3)—K(1)	160·1 (11)
S(4)—C(4)—N(4)	177·3 (12)	N(1)—K(1)—N(3)	64·4 (3)
N(1)—K(1)—O(11)	134·3 (3)	N(3)—K(1)—O(11)	79·5 (3)
N(1)—K(1)—O(14)	125·7 (2)	N(3)—K(1)—O(14)	70·6 (3)
O(11)—K(1)—O(14)	58·5 (2)	N(1)—K(1)—O(21)	96·6 (2)
N(3)—K(1)—O(21)	90·9 (3)	O(11)—K(1)—O(21)	111·7 (2)
O(14)—K(1)—O(21)	54·6 (2)	N(1)—K(1)—O(24)	76·7 (2)
N(3)—K(1)—O(24)	128·7 (3)	O(11)—K(1)—O(24)	148·5 (2)
O(14)—K(1)—O(24)	112·6 (2)	O(21)—K(1)—O(24)	60·8 (2)
N(1)—K(1)—O(27)	88·4 (2)	N(3)—K(1)—O(27)	145·2 (3)
O(11)—K(1)—O(27)	109·6 (2)	O(14)—K(1)—O(27)	143·3 (2)
O(21)—K(1)—O(27)	114·6 (2)	O(24)—K(1)—O(27)	57·3 (2)
N(1)—K(1)—O(34)	112·1 (3)	N(3)—K(1)—O(34)	115·8 (3)
O(11)—K(1)—O(34)	59·0 (2)	O(14)—K(1)—O(34)	113·9 (2)
O(21)—K(1)—O(34)	146·9 (2)	O(24)—K(1)—O(34)	108·9 (2)
O(27)—K(1)—O(34)	53·0 (2)	N(2)—K(2)—O(41)	88·8 (2)
N(2)—K(2)—O(44)	98·6 (3)	O(41)—K(2)—O(44)	60·9 (2)
N(2)—K(2)—O(51)	104·3 (3)	O(41)—K(2)—O(51)	116·0 (2)
O(44)—K(2)—O(51)	55·3 (2)	N(2)—K(2)—O(54)	100·4 (2)
O(41)—K(2)—O(54)	170·7 (2)	O(44)—K(2)—O(54)	116·2 (2)
O(51)—K(2)—O(54)	61·2 (2)	N(2)—K(2)—O(57)	94·6 (2)
O(41)—K(2)—O(57)	118·5 (2)	O(44)—K(2)—O(57)	166·7 (2)
O(51)—K(2)—O(57)	122·2 (2)	O(54)—K(2)—O(57)	61·9 (2)
N(2)—K(2)—O(64)	89·9 (3)	O(41)—K(2)—O(64)	62·5 (2)
O(44)—K(2)—O(64)	122·5 (2)	O(51)—K(2)—O(64)	165·8 (2)
O(54)—K(2)—O(64)	117·8 (2)	O(57)—K(2)—O(64)	56·1 (2)

Atomic coordinates are given in Table 1, details of selected interatomic distances and angles in Table 2.*

Discussion. The structure of the molecule is shown in Fig. 1. The tetrathiocyanatomercurate(II) anion consists of a slightly distorted HgS_4 tetrahedron with S—Hg—S bond angles in the range 98·0 (1) to 126·8 (1)°. The thiocyanate groups are essentially linear with deviation from linearity of about 2° in the S—C—N angles. However, the Hg—S—C angles vary from 92·9 (5) to 99·9 (4)°. Hg—S bond lengths fall in the range between 2·497 (3) and 2·591 (3) Å with an average of 2·543 (44) Å. For the thiocyanate groups the S—C distances are within the range 1·647 (13) to 1·689 (13) Å with an average of 1·668 (16) Å, while the C—N bond lengths vary from 1·155 (15) to 1·175 (18) Å with an average of 1·165 (8) Å. All the above data are in agreement with the corresponding values found in compounds containing the tetrathiocyanatomercurate(II) anion (Brodersen & Hummel, 1982; Jeffrey & Rose, 1968; Udupa & Krebs, 1980).

The coordination environments around the two potassium ions are different. K(1) has a coordination number of eight, being coordinated to two N atoms from the same tetrathiocyanatomercurate(II) anion and six O atoms from a dibenzo-18-crown-6 macrocycle. K(1)···N(1) and K(1)···N(3) distances are 2·961 (11) and 2·924 (11) Å while the K···N—C angles are 159·0 (8) and 160·1 (11)° respectively. The K···N distances are slightly longer than those reported for some potassium thiocyanate–crown ether complexes (Larson & Dalley, 1982). This is a consequence of the fact that the two coordinating N atoms are on the same side of the O_6 plane. K(1)···O distances vary from 2·789 (7) to 2·932 (7) Å with an average of 2·842 (50) Å. These distances are consistent with an eight-coordinated potassium ion (Nagano, 1979), which as a result lies 0·83 (2) Å from the O_6 plane. Within the crown ether the average aliphatic and aromatic C—C bond lengths are 1·503 (11) and 1·379 (16) Å respectively, while the average O—C (aliphatic) and O—C (aromatic) distances are 1·432 (12) and 1·378 (7) Å respectively.

In the case of the second potassium ion, which is seven-coordinated, the K(2)···N(2) distance is 2·727 (11) Å and the K(2)···N(2)—C(2) angle is 172·0 (8)°. K(2) is only 0·29 (2) Å from the oxygen plane of the macrocycle with K···O distances in the range between 2·746 (7) and 2·796 (7) Å for an average of 2·764 (17) Å. The geometry about K(2) is therefore hexagonal pyramidal. Average aliphatic C—C, aromatic C—C, O—C (aliphatic) and O—C (aromatic) distances in the macrocycle are 1·508 (13), 1·385 (21), 1·439 (12) and 1·377 (13) Å respectively, in agreement with corresponding values reported.

The solvent ethanol molecule in the crystal is disordered. It appears to have one principal location denoted by C(72)—C(71)—O(70) (half-occupancy). A second half-occupancy site is disordered between

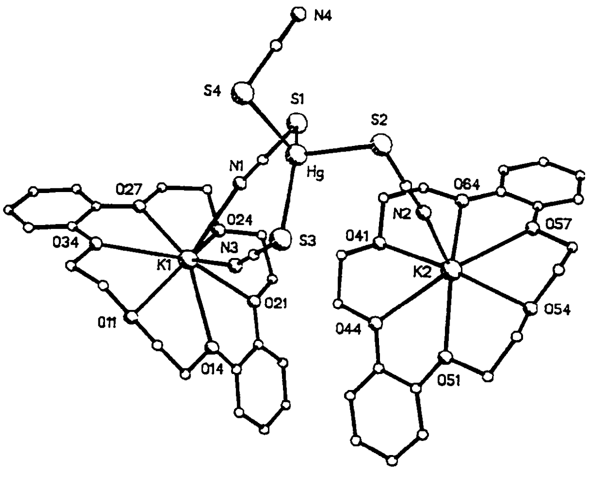

Fig. 1. Diagram showing the molecule with the solvate omitted.

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* Lists of structure factors, anisotropic thermal parameters, bond lengths, bond angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51412 (49 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

C(81)′–C(81)–O(80) and C(81)–C(81)′–O(80)′. The presence of the solvent molecule did not significantly affect the refinement of the crystal structure.

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Structure of Tetrakis{[1-(phenyltriazene-1,3-diyl)-2-(phenyltriazenyl)benzene]copper(I)}

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Abstract. $[\{C_6H_5NNNC_6H_4NNN(H)C_6H_5\}Cu]_4$, $M_r = 1515{\cdot}60$, orthorhombic, *Pbcn*, $a = 20{\cdot}552\,(2)$, $b = 18{\cdot}996\,(3)$, $c = 17{\cdot}140\,(3)$ Å, $V = 6691{\cdot}4$ Å^3, $Z = 4$, $D_x = 1{\cdot}504$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54184$ Å, $\mu = 19{\cdot}028$ cm^{-1}, $F(000) = 3104$, $T = 293$ K. The final R value is 0·058 for 2319 significant $[I > 3\sigma(I)]$ reflections. In the tetrameric complex of site symmetry 2 each Cu atom of the distorted Cu_4 rhombus is bonded to two *ortho* N atoms and to one N atom of the bridging N1, N3 function of the ligands. The Cu···Cu distances are 2·650 (2) and 2·684 (2) Å, respectively.

Introduction. Triazeno ligands in metal complexes are monodentate, (*N*1,*N*3)-chelating and bridging (Moore & Robinson, 1986); (*N*1,*N*1)- and (*N*1,*N*2)-bridges and coordination *via* N2 or an η^3-structure similar to the η^3-allyl complexes have not yet been observed. We synthesized a new bis(triazene) ligand with both N_3 units in one molecule to extend the possibilities of coordination and to force close contacts between metal atoms.

Experimental. The reaction of 1,2-bisphenyltriazenobenzene with $Cu(NH_3)_4Cl$ in ether/methanol yields dark red crystals of the title compound. The parameters for intensity-data collection, structure solution and refinement are listed in Table 1. The final atomic coordinates are given in Table 2, selected bond distances and angles in Table 3.* Figs. 1 and 2 show the numbering scheme and a stereoview, respectively.

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* Lists of structure factors, anisotropic thermal parameters, planes, further distances and angles, and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51373 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.