hydride intermediates in these reactions. In a slightly earlier report, Ginsberg[39] had mentioned that the polyhydride anion $[ReH_8(PPh_3)]^-$ was converted to $(Ph_3PH)_2Re_2Cl_8$ upon treatment with HCl. The "deficiency" of phosphine ligand in this anion (compared to $ReH_7(PR_3)_2$) clearly has a dramatic effect on this reaction, but it is not obvious why the alternative reaction $[ReH_8(PPh_3)]^- + 5HCl \rightarrow [ReCl_5(PPh_3)]^- + 6.5H_2$ does not occur. Nonetheless, this reaction constituted an interesting early example of a single step conversion of a mononuclear complex to a multiply bonded dinuclear species.[11] In the present study, we have taken the opportunity to carry out the analogous reaction between $Re_2H_8(PPh_3)_4$ and gaseous HCl. To our surprise, this turned out to afford an unusual species, the major product being the mixed salt $(Ph_3PH)_2Re_2Cl_8{\cdot}5(Ph_3PH)ReCl_5(PPh_3)$ containing both mononuclear Re(IV) and dinuclear Re(III) components. Separation and purification of the two components can be accomplished by treating the crystals with dichloromethane. The explanation for this reaction is not obvious, although it is in accord with other work that has shown that nonhydridic products are the rule.[14,39-41]

Reactions of the Salts $(Ph_3PC_3H_5)_2Re_2X_8$ and $(Ph_3PC_3H_5)_2ReI_6$ with Triphenylphosphine and Acetic Acid-Acetic Anhydride. The complexes $(Ph_3PC_3H_5)_2Re_2X_8$ (X = Cl or Br) react in the predicted fashion[11] with PPh_3 and with $CH_3CO_2H-(CH_3CO)_2O$ to give the quadruply bonded dirhenium(III) species $Re_2X_6(PPh_3)_2$ and $Re_2(O_2CCH_3)_4X_2$, respectively. In other words, retention of the quadruple bond is observed. At the time when we first reacted $Re_2H_8(PPh_3)_4$ with allyl iodide, we had anticipated that the product would be $(Ph_3PC_3H_5)_2Re_2I_8$. Accordingly, when we first began to characterize this material and reacted it with refluxing acetic acid-acetic anhydride, our isolation of $Re_2(O_2CCH_3)_4I_2$ did not surprise us. Later, when we realized that the correct formulation was $(Ph_3PC_3H_5)_2ReI_6$ rather than $(Ph_3PC_3H_5)_2Re_2I_8$, it became apparent that the formation of $Re_2(O_2CCH_3)_4I_2$ constituted a relatively rare example of the reductive coupling of two higher oxidation state rhenium centers to give a dinuclear multiply bonded species. The conversion of *trans*-$ReOX_3(PPh_3)_2$ (X = Cl or Br) to $Re_2(O_2CCH_3)_4X_2$ is another such example.[18]

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Registry No. $Re_2H_8(PPh_3)_4$, 66984-37-0; $ReH_7(PPh_3)_2$, 12103-40-1; $ReH_5(PPh_3)_2C_6H_{11}NH_2$, 25702-61-8; $ReH_5(PPh_3)_2C_5H_{10}NH$, 25702-62-9; $MoH_4(PMePh_2)_4$, 32109-07-2; $Re_2Cl_6(PPh_3)_2$, 11087-98-2; $(Ph_3PC_3H_5)_2ReCl_6$, 85319-88-6; $(Ph_3PC_3H_5)_2ReBr_6$, 85335-12-2; $(Ph_3PC_3H_5)_2ReI_6$, 85335-13-3; $(Ph_3PC_3H_5)_2Re_2Cl_8$, 85335-14-4; $(Ph_3PC_3H_5)_2Re_2Br_8$, 85335-15-5; $ReH_5(PPh_3)_2(H_2NC_3H_5)$, 85319-89-7; *trans*-$ReCl_4(PPh_3)_2$, 34248-10-7; $(Ph_4As)_2Re_2Cl_8$, 14649-98-0; $(Ph_3PH)_2Re_2Cl_8{\cdot}5(Ph_3PH)ReCl_5(PPh_3)$, 85335-17-7; $(Ph_3PH)ReCl_5(PPh_3)$, 36550-27-3; $(Ph_3PH)_2Re_2Cl_8$, 83511-36-8; $NH_2C_3H_5$, 107-11-9; CCl_4, 56-23-5; $CHCl_3$, 67-66-3; CH_2Cl_2, 75-09-2; $(CH_3)_3CCl$, 507-20-0; C_6H_5Cl, 108-90-7; HCl, 7647-01-0; PPh_3, 603-35-0; C_3H_5Cl, 107-05-1; C_3H_5Br, 106-95-6; C_3H_5I, 556-56-9; C_3H_5NCS, 764-49-8; CH_3CO_2H, 64-19-7; Re, 7440-15-5.

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Crystal Structure of Tris(2,5-dimethyl-2,5-diisocyanohexane)disilver(I) Diperchlorate: A Unidimensional, Ladderlike, Polymeric Metal Complex

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Reaction of $AgClO_4$ with 2,5-dimethyl-2,5-diisocyanohexane (TMB) in methanol/acetonitrile gives rise to colorless crystals of $[Ag_2(TMB)_3](ClO_4)_2$, which were investigated by X-ray diffraction. The complex belongs to the triclinic space group $P\bar{1}$, $a = 8.951$ (5) Å, $b = 9.018$ (9) Å, $c = 15.500$ (10) Å, $\alpha = 93.54$ (7)°, $\beta = 90.73$ (5)°, $\gamma = 115.86$ (6)°, and $Z = 1$. The structure consists of pairs of $\cdots\mathrm{Ag{-}C}\overline{\mathrm{N\ N}}\mathrm{C{-}Ag{-}C}\overline{\mathrm{N\ N}}\mathrm{C{-}Ag}\cdots$ infinite chains containing the TMB ligand in an extended form. Pairs of chains are cross-linked at every step by another TMB ligand joining a silver atom in one chain to the corresponding silver on the opposite chain. Each silver atom is thus bonded to three CN groups defining a distorted-trigonal plane. The Ag-CN distances (average 2.14 Å) are significantly longer than in the rhodium complex (average 1.94 Å). A weak interaction with one oxygen of the perchlorate anion is also apparent (Ag-O = 2.73 (1) Å). The complex is slightly soluble in acetonitrile, and its ^{13}C NMR spectrum has been obtained.

Introduction

Diisocyanide ligands are of special interest due to their versatility in bonding with metal complexes and to their ability to give rise to complexes with unusual properties.[2-4] The differences in bonding may be related to the design of the diisocyanide ligand (geometrical requirements imposed by the relative location of the two isocyanide groups, nature of the bridge), as well as to the nature of the metal atom and of the remaining ligands.

Until now, few well-characterized diisocyanide metal complexes have been reported. Gray et al.[5,6] have shown by x-ray crystallography that 2,5-dimethyl-2,5-diisocyanohexane (TMB = "tetramethyl bridge") gives rise to a ligand-bridged dinuclear cationic complex $[Rh_2(TMB)_4](PF_6)_2{\cdot}2CH_3CN$ when reacting with a Rh(I) complex and to a cubane-like structure $[Ni_4(OCH_3)_4(TMB)_4(OAc)_2](BPh_4)_2$ when reacting with Ni(O-

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Ac)$_2$ in methanol. A tetranuclear structure has also been reported for $H_3(Rh_4(bridge)_8Cl)(CoCl_4)_4{\cdot}xH_2O$ (bridge = 1,3-diisocyanopropane).[7] Therefore, it was interesting to see if the diisocyanide ligand would be able to bring together two metal atoms that do not normally form a metal–metal bond but can easily be positioned side by side by chelating ligands. Silver fills these two requirements since dinuclear Ag complexes without Ag–Ag bonds have been reported for chelating ligands such as trifluoroacetate,[8] adenine,[9] and others.[10] In the present paper, we report the X-ray structural characterization of the $[Ag_2(TMB)_3](ClO_4)_2$ compound, in which the TMB ligand is in its extended form and generates a unidimensional polymeric material. This complex is slightly soluble in acetonitrile, and its $^{13}C\{^1H\}$ NMR spectrum is described.

Experimental Section

Standard procedures were used to prepare 2,5-dimethyl-2,5-diisocyanohexane (TMB).[11]

The $^{13}C\{^1H\}$ NMR spectrum was recorded at 22.63 MHz by using a Bruker HX-90 with ^2D as an internal lock and complete ^1H decoupling. It was referenced to $Si(CH_3)_4$. The sample was prepared with CH_3CN/CD_3OD as the solvent.

IR spectra were recorded on a Perkin-Elmer 137 spectrophotometer as Nujol mulls between KBr disks. The electronic spectrum was obtained on a Cary 14 spectrophotometer in acetonitrile.

$[Ag_2(TMB)_3](ClO_4)_2$. TMB (0.99 g; 6 mM) dissolved in 30 mL of acetonitrile was added quickly to a methanol solution of $Ag(ClO_4){\cdot}H_2O$ (1.35 g; 6 mM; 30 mL). After 30 min, the solution was concentrated to 30 mL. At −30 °C, colorless parallelepipeds separated. They were collected on a frit and washed with cold ether. They were suitable for X-ray investigation. Anal. Calcd for $C_{30}H_{48}Ag_2Cl_2N_6O_8$: C, 32.5; H, 4.33; N, 7.58. Found: C, 33.8; H, 4.93; N, 7.69.

Crystal Data: $C_{30}H_{48}Ag_2Cl_2N_6O_8$, fw = 907.39, triclinic, space group $P\bar{1}$, $a = 8.951$ (5) Å, $b = 9.018$ (9) $c = 15.500$ (10) Å, $\alpha = 93.54$ (7)°, $\beta = 90.73$ (5)°, $\gamma = 115.86$ (6)°, $V = 1122.8$ Å^3, $Z = 1$, $D_{calcd} = 2.683$ g cm^{-3}, λ(Cu K$\tilde{\alpha}$) = 1.541 78 Å, $T = 22$ °C, μ(Cu Kα) = 172.5 cm^{-1}.

Crystallographic Measurements. A well-formed, transparent crystal was selected for X-ray work. Its dimensions were as follows: 0.24 mm (between faces 001 and 00$\bar{1}$) × 0.082 mm (0$\bar{1}$1 and 01$\bar{1}$) × 0.23 mm (1$\bar{1}$1 and $\bar{1}$1$\bar{1}$). Precession films failed to show any Laue symmetry higher than $\bar{1}$, and a triclinic reduced cell was defined. The crystal was transferred to an Enraf-Nonius CAD4 diffractometer. A list of 25 reflections was created by the SEARCH procedure, and these reflections were centered several times in the counter aperture. The autoindexing routine of the CAD4 software yielded the cell originally deduced from film work. The Niggli parameters clearly indicated that the crystal could not be described with a lattice of higher symmetry.

The intensity data were collected by using the $\omega/2\theta$ scan technique. A fixed slit of 4.0 mm was used, and the scan width ($\omega = 1.10 + 0.14 \tan\theta$) was extended 25% on each side for background. Fast prescans at 10° min^{-1} were made for each reflection, and all the weak ones ($I < \sigma(I)$) were not remeasured at slower speed. The stronger reflections were measured at a scan speed S between 10.0 and 1.1° min^{-1}, the value being selected to make the $I/\sigma(I)$ ratio equal to 100, but the scan time was limited to 90 s. Three standard reflections were measured every hour as a check on crystal and instrument stability. They showed random fluctuations of <±3.8% about their respective means. Crystal orientation was also checked every 100 measurements. The difference between the actual orientation of the reciprocal vector and the direction deduced from the orientation matrix was always <0.10°, which made any crystal recentering unnecessary.

The net intensity I for each reflection was obtained from $I = (P - 2B)S$, where P is the scan count and B is the total background, counted during half of the scanning time. The variance was calculated from $\sigma(I)^2 = (P + 4B)S^2 + (0.04I)^2$.

A set of 4188 independent reflections (hkl, $hk\bar{l}$, $h\bar{k}l$, and $h\bar{k}\bar{l}$) in a reflection sphere limited by $2\theta \le 140°$ was collected. On the basis of the criterion $I < 3.0\sigma(I)$, 2031 measurements were rejected as not being significantly above background. The set of 2157 nonzero reflections was used to solve and refine the structure. These data were corrected for the effects of Lorentz, polarization and absorption effects (Gaussian integration, grid 8 × 8 × 8, transmission coefficient = 0.15–0.55).

Resolution of the Structure and Refinement. The structure was solved by the heavy-atom method and refined by full-matrix least squares in the early stages. The Ag atom was located from a Patterson synthesis, and the remaining non-hydrogen atoms were positioned from subsequent different Fourier (ΔF) maps. Isotropic refinement of all non-hydrogen atoms led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.15$. After a few cycles, in which Ag was refined anisotropically, the calculated ΔF map showed peaks of ~2 e Å^{-3} close to O2, O3, and O4. These peak positions, together with the much higher thermal motion of these oxygens compared to the motion of O1, were consistent with the ClO_4 ions being disordered over two orientations ~60° apart about the Cl–O1 bond. Thus, Cl and O1 were described as ordered atoms, while the rest of the ion was defined as six half-oxygens O2–O7. These individual components behaved normally in the subsequent cycles of refinement. A new ΔF map contained peaks of 0.4–0.9 e Å^{-3} at suitable positions for hydrogen atoms. Those of the methylene groups (C3 and C4) were fixed at their ideal positions ($B = 7.5$ Å^2). At least one hydrogen peak was found for each methyl group, and these known positions were used to calculated those of the missing hydrogens. The latter were assigned a B value of 8.5 Å^2, and they were not refined.

In the last cycles of refinement, individual weights based on counting statistics were applied and the block-diagonal approximation was used. All the non-hydrogen atoms were anisotropically refined, and the methyl hydrogens located on the ΔF map were isotropically refined. The positions of the fixed hydrogen atoms were recalculated after each cycle. At the very end, it was noted that one set of disordered perchlorate oxygens had greater thermal motion. A few more cycles of refinement were calculated in which individual occupancy factors were refined for these oxygens, simultaneously with all the parameters mentioned above. The occupancy factors converged to 0.58 (6) for O2, O3, and O4 and to 0.30 (6) for O5, O6, and O7. Therefore, the occupancy factors were fixed at the normalized values (0.667 and 0.333) and a few more cycles were run to terminate the refinement. The final R value was 0.058. The weighted residual $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ was 0.069. The goodness-of-fit ratio was 2.22.

In the final ΔF map, the highest peaks (0.4–0.8 e/Å^3) were found near Ag or the disordered oxygen atoms. The general background was <±0.35 e/Å^3. The map did not contain indications leading to the belief that the space group could be $P1$ instead of $P\bar{1}$.

The form factors used were those of Cromer and Waber[12] except for hydrogen.[13] The f' and f'' contributions to anomalous dispersion were taken into account for Ag and Cl.[14] The programs used in this work are listed elsewhere.[15]

The refined positional parameters are listed in Table I. The anisotropic temperature factors and the list of observed and calculated structure factors amplitudes are part of the supplementary material.

Results and Discussion

$[Ag_2(TMB)_3](ClO_4)_2$ is a colorless crystalline complex slightly soluble in acetonitrile. Its IR spectrum shows a strong ν(CN) band at 2170 cm^{-1} in the solid state (free TMB ligand: ν(CN) = 2120 cm^{-1}).

The room-temperature (33 °C) proton-decoupled FT ^{13}C NMR spectrum of a solution of $[Ag_2(TMB)_3](ClO_4)_2$ in CH_3CN/CD_3OD is shown in Figure 1. It consists of the resonances of the solvents (two strong lines at δ 2.30 (CH_3) and 119.50 (CN) assigned to CH_3CN; a septuplet at δ 50 ppm assigned to CH_3OH) and of three singlets of decreasing in-

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Table I. Refined Positional Parameters ($\times 10^4$, H $\times 10^3$)

atom	x	y	z
Ag	4693 (1)	968 (1)	2324 (1)
Cl	1612 (3)	2621 (4)	2992 (2)
O1	1989 (14)	1249 (13)	2964 (8)
O2[a]	2141 (24)	3326 (28)	2211 (12)
O3[a]	2212 (23)	3469 (23)	3744 (10)
O4[a]	−138 (18)	1969 (26)	2913 (13)
O5[b]	3091 (33)	3920 (37)	3051 (26)
O6[b]	684 (39)	2553 (38)	3686 (24)
O7[b]	625 (47)	3037 (56)	2416 (18)
N1A	5507 (9)	8732 (9)	3692 (5)
N2A	7583 (9)	4702 (10)	2832 (5)
N1B	2613 (10)	−297 (12)	454 (5)
C1A	5065 (13)	9343 (14)	3180 (7)
C2A	6154 (11)	8113 (12)	4382 (6)
C3A	6774 (13)	6884 (13)	3990 (7)
C4A	8056 (13)	7480 (14)	3313 (9)
C5A	8881 (13)	6366 (14)	3067 (8)
C6A	6529 (12)	3413 (14)	2637 (7)
C7A	7549 (13)	9634 (15)	4860 (7)
C8A	4768 (13)	7263 (14)	4984 (7)
C9A	9906 (18)	6948 (19)	2311 (12)
C10A	9864 (18)	6209 (20)	3802 (12)
C1B	3361 (13)	124 (14)	1102 (7)
C2B	1601 (13)	−845 (16)	−363 (7)
C3B	−60 (13)	−829 (15)	−177 (7)
C7B	1379 (18)	−2562 (21)	−605 (10)
C8B	2554 (17)	354 (23)	−1028 (8)
H31A[c]	724	655	445
H32A[c]	584	595	373
H41A[c]	753	760	281
H42A[c]	890	853	352
H71A	690 (16)	1015 (17)	503 (9)
H72A	810 (11)	917 (11)	532 (6)
H73A	827 (8)	1022 (9)	447 (5)
H81A[c]	399	640	460
H82A	438 (9)	797 (10)	527 (5)
H83A	522 (10)	693 (11)	557 (6)
H91A[c]	1027	616	209
H92A	1085 (17)	796 (18)	255 (9)
H93A[c]	931	717	187
H101A[c]	1085	720	394
H102A	1009 (9)	537 (9)	357 (5)
H103A[c]	923	590	430
H31B[c]	−72	−115	−70
H32B[c]	−59	−161	23
H71B[c]	131	−280	−121
H72B	41 (16)	−312 (17)	−36 (9)
H73B[c]	224	−277	−36
H81B	188 (11)	5 (11)	−153 (6)
H82B	269 (13)	144 (13)	−73 (7)
H83B[c]	359	39	−119

[a] Occupancy factor 0.67. [b] Occupancy factor 0.33. [c] Not refined.

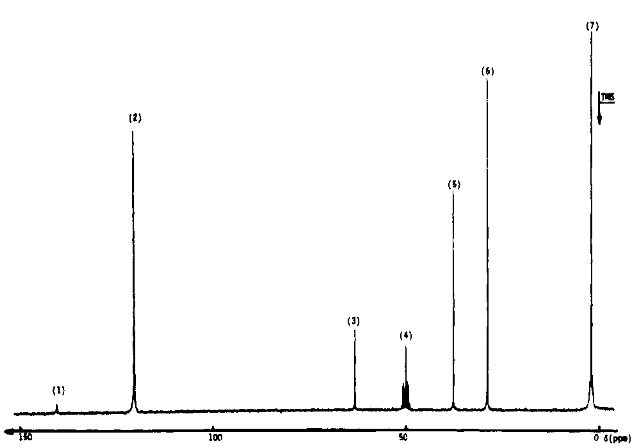

Figure 1. Room-temperature $^{13}C\{^1H\}$ FT NMR spectrum of $[Ag_2(TMB)_3](ClO_4)_2$ in CH_3CN/CD_3OD: (2) and (7) CH_3CN; (4) CD_3OD; (1), (3), (5), and (6) TMB.

Table II. Interatomic Distances and Bond Angles

	Distances (Å)		
Ag–C1A[a]	2.162 (12)	Ag–C1B	2.136 (11)
Ag–C6A	2.118 (12)	Ag–O1	2.733 (13)
C1A–N1A	1.152 (14)	N1B–C2B	1.474 (14)
N1A–C2A	1.460 (13)	C2B–C3B	1.524 (19)
C2A–C3A	1.539 (16)	C2B–C7B	1.495 (21)
C2A–C7A	1.532 (16)	C2B–C8B	1.521 (20)
C2A–C8A	1.512 (16)	C3B–C3B[b]	1.518 (17)
C3A–C4A	1.506 (17)	Cl–O1	1.416 (12)
C4A–C5A	1.519 (18)	Cl–O2	1.393 (20)
C5A–N2A	1.461 (15)	Cl–O3	1.322 (17)
C5A–C9A	1.474 (22)	Cl–O4	1.413 (20)
C5A–C10A	1.482 (22)	Cl–O5	1.33 (3)
N2A–C6A	1.151 (14)	Cl–O6	1.36 (4)
C1B–N1B	1.147 (14)	Cl–O7	1.42 (4)
	Angles (deg)		
C1A[a]–Ag–C6A	108.8 (4)	C6A–Ag–C1B	124.1 (4)
C1A[a]–Ag–C1B	123.2 (4)	C6A–Ag–O1	99.4 (4)
C1A[a]–Ag–O1	103.1 (4)	C1B–Ag–O1	88.3 (4)
Ag–O1–Cl	129.2 (7)	N1B–C1B–Ag	177.5 (10)
N1A–C1A–Ag[c]	167.7 (10)	C1B–N1B–C2B	178.1 (11)
C1A–N1A–C2A	174.6 (10)	N1B–C2B–C3B	106.8 (10)
N1A–C2A–C3A	109.6 (8)	N1B–C2B–C7B	106.5 (11)
N1A–C2A–C7A	106.1 (8)	N1B–C2B–C8B	107.2 (10)
N1A–C2A–C8A	108.3 (8)	C3B–C2B–C7B	111.0 (11)
C3A–C2A–C7A	112.4 (9)	C3B–C2B–C8B	112.7 (11)
C3A–C2A–C8A	110.1 (9)	C7B–C2B–C8B	112.2 (12)
C7A–C2A–C8A	110.1 (9)	C2B–C3B–C3B[b]	114.8 (10)
C2A–C3A–C4A	117.4 (10)	O1–Cl–O2	104.6 (10)
C3A–C4A–C5A	115.9 (10)	O1–Cl–O3	107.2 (10)
C4A–C5A–N2A	108.5 (10)	O1–Cl–O4	106.4 (10)
C4A–C5A–C9A	110.5 (11)	O2–Cl–O3	121.6 (12)
C4A–C5A–C10A	112.2 (12)	O2–Cl–O4	103.9 (12)
N2A–C5A–C9A	108.1 (11)	O3–Cl–O4	112.0 (12)
N2A–C5A–C10A	106.0 (11)	O1–Cl–O5	104.0 (16)
C9A–C5A–C10A	111.3 (12)	O1–Cl–O6	108.6 (16)
C5A–N2A–C6A	177.8 (11)	O1–Cl–O7	130.9 (18)
N2A–C6A–Ag	175.8 (10)	O5–Cl–O6	113.2 (21)
		O5–Cl–O7	105.3 (22)
		O6–Cl–O7	94.8 (22)

[a] $x, -1 + y, z$. [b] $-x, -y, -z$. [c] $x, 1 + y, z$.

tensity assigned to the different carbon atoms of the TMB bridge. The four CH_3 group are located at δ 29.12 (free TMB at δ 29.89), the two CH_2 groups at δ 37.71 (free, 37.82), the two $C-(CH_3)_2$ carbons at δ 62.90 (free, 57.60), and the two C≡N carbons at δ 139.39 (free, 155.3). Thus, coordination to silver is characterized by an increase in shielding of the CN carbon ($\Delta\delta = -15.9$) and a decrease for the $C-(CH_3)_2$ carbon ($\Delta\delta = 5.3$), indicating that the latter carbons are perturbed by the bonding.

The solid-state structure of the complex is shown in Figure 2,and the numbering scheme is given in Figure 3. The TMB molecule does not assume an assembling role in the present compound. The structure consists of pairs of ···Ag—CN NC—Ag—CN NC—Ag··· infinite chains (ligands A) containing the diisocyanide molecule in an extended form. Pairs of chains are cross-linked at every step, by another TMB ligand (B) joining a silver atom in one chain to the corresponding one in the opposite chain. Schematically, this pattern can be compared to a ladder in which the side pieces would be infinite chains and the rungs would correspond to the cross-linking ligands. Each silver atom also forms an extra bond with a more distant perchlorate oxygen.

The interatomic distances and bond angles are listed in Table II. The Ag–CN bonds (average 2.14 Å) are similar to those found in $K[Ag(CN)_2]$ (2.13 Å)[16] and longer than

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(16) Wells, A. F. "Structural Inorganic Chemistry"; Oxford University Press: London, 1962; p 737.

Table III. Torsion Angles (deg) in the TMB Ligand

bonds	ligand A (this work)	ligand B (this work)	$[Rh_2(TMB)_4](PF_6)_2$[5]	$[Ni_4(OMe)_4(OAc)_2(TMB)_4](BPh_4)_2$[6]		
N1-C2-C3-C4	55.8	57.4	64.1	64.1	62.6	68.6
C2-C3-C4-C5	168.6	180.0	−147.0	−143.7	−141.6	−147.3
N2-C5-C4-C3	52.8	−57.4	64.1	67.0	62.6	68.6

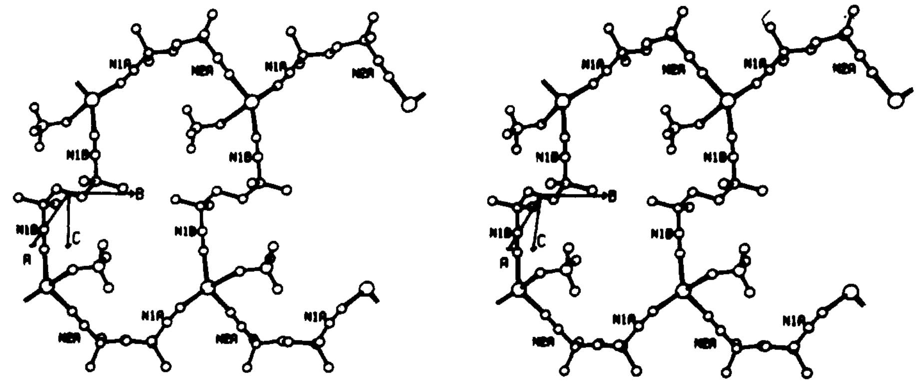

Figure 2. Stereoview of the infinite ladderlike pattern in the crystal. Silver is represented by larger spheres, and the tetrahedral ClO_4^- ions bound to Ag by O1 are easily recognized. The carbon atoms can be identified by comparison with Figure 3.

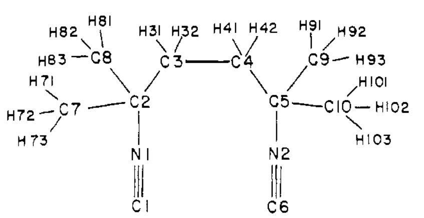

Figure 3. Numbering scheme in the TMB ligand. The hydrogens are identified by a two-digit number, the first of which is the same as the carbon atom to which it is attached (e.g. H81, H82, and H83 are attached to the C8 methyl carbon). Corresponding atoms in the two independent ligands are distinguished by the letter A or B.

those observed for the Rh(I) species (average 1.95 Å) and the Ni(II) complex (average 2.07 Å). The C≡N bond length of 1.15 Å (average) is not significantly different from the usual value of 1.16 Å. Departure from linearity is observed essentially for ligand A at N1A and C1A (C2A-N1A-C1A = 174.6 (10)°; N1A-C1A-Ag = 167.7 (10)°), whereas the corresponding angles at N1B and C1B (ligand B) and at N2 and C6 in both ligands are normal (Table II).

The remaining bond lengths in the TMB ligands are also normal and do not differ significantly from those reported for the rhodium and nickel complexes. Their average values are as follows (Å): $N-C(Me_2) = 1.46$; $C(Me_2)-C(H_2) = 1.53$; $C(H_2)-C(H_2) = 1.52$; C–Me = 1.50; $\sigma = 0.01-0.02$ Å.

The three Ag–CN bonds define around each Ag atom a distorted-trigonal plane (C–Ag–C = 124.1, 123.2, 108.8; $\sigma = 0.4°$) with the metal only 0.25 Å above the plane in the direction of O1. The Ag–O1 interaction, although not negligible, is definitively much weaker than the bonds to isocyanide. The distance (2.73 (1) Å) is about halfway between the short Ag–O contacts of 2.34–2.45 Å found in salts with oxyanions (NO_3^-, ClO_4^-)[17,18] and the 3.0-Å limit above which the interactions are believed to become vanishingly small.[19] Thus, silver should be described as (3 + 1)-coordinated with a trigonal-pyramidal geometry.

The ClO_4 anion is disordered, but as a result of the Ag–O1 interaction, the Cl–O1 bond is not involved in the disorder. Such a situation has already been observed in other silver–perchlorate compounds.[18,19] The three remaining oxygens form only weak van der Waals contacts with methyl hydrogens belonging to various chains. The electron density map was interpreted in terms of two unequal populations related by a ~60° rotation about Cl–O1. The refinement of such a model is not expected to lead to perfect atomic positions, and some distorsion is indeed observed (Table II). However, exact positioning of the free perchlorate oxygens is not critical for this structure.

Thus, in contrast with the case for rhodium and nickel compounds in which the isocyano groups are so oriented that they can bridge a pair of metal atoms, the TMB ligands in the present structure are in extended form with the C≡N—C groups pointing in opposite directions. Various rotamers can be generated by rotation about the $C(H_2)-C(H_2)$ bond and the two $C(H_2)-C(Me_2)$ bonds. The corresponding torsion angles for the two independent molecules of this structure, the three molecules in the Ni compound,[6] and the nondisordered ligand in the Rh compound[5] are listed in Table III. Obviously, the methyl groups force the $N-C(Me_2)$ and the $C(H_2)-C(H_2)$ bonds to adopt one of the two possible gauche orientations ($\tau = +60$ or $-60°$). This is probably a rather rigid parameter in the chain conformation, since the range is only ±8° in the available data. Therefore, the $C(H_2)-C(H_2)$ bond is the soft region of the ligand. In the Ag compound, one ligand is perfectly trans by symmetry, while the other is 11° away from this conformation. These approximate staggered orientations should be sterically favored. In the Rh and Ni compounds, the $C(H_2)-C(Me_2)$ bonds are in a gauche orientation and the ligand is not expected to adopt spontaneously this conformation in the free state. For this reason, it may be difficult to make TMB assume an assembling role in a system where the precursor metal species did not contain a pair of bonded or close metal atoms.

Registry No. $[Ag_2(TMB)_3](ClO_4)_2$, 85152-43-8.

Supplementary Material Available: Listings of refined temperature factors (Table IV), distances and angles involving the hydrogen atoms (Table V), equations of the least-squares planes (Table VI), and observed and calculated structure factor amplitudes (Table VII) (20 pages). Ordering information is given on any current masthead page.

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