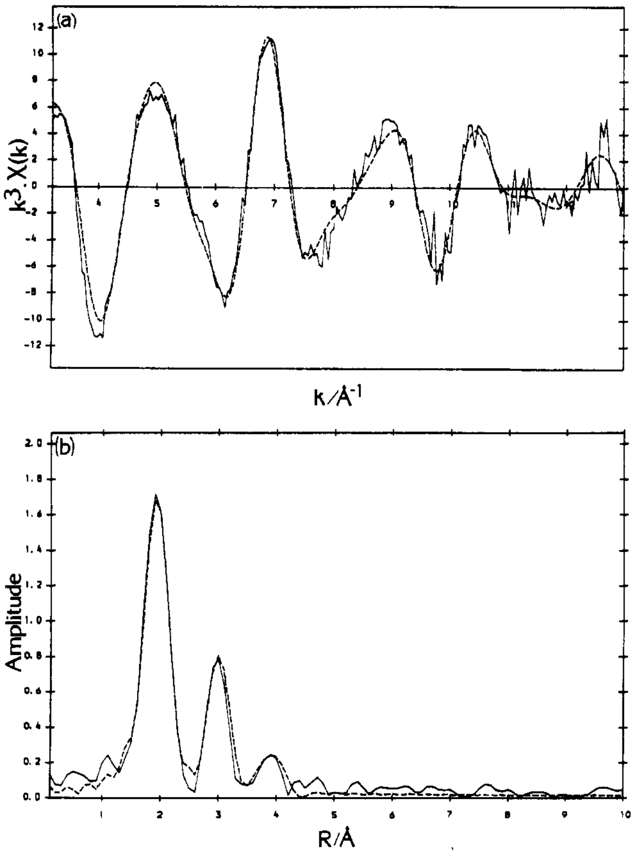

Figure 1. Cr K-edge EXAFS data of the chromium ion exchanged bentonite at room temperature: (a) k^3-weighted EXAFS and (b) the Fourier transform, phase-shift corrected for oxygen. Key: (—) experiment and (--) spherical wave theory for six O at 1.97 Å, two Cr at 2.97 Å, and two Cr at 3.90 Å gives a fit with $R = 20\%$.

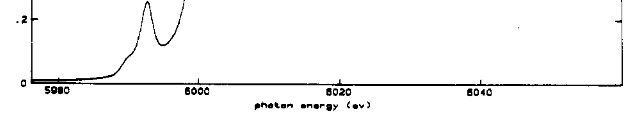

Figure 2. Cr K-edge XAS near-edge structure of the chromium ion exchanged bentonite recorded at room temperature after being calcined at 250 °C.

a series of samples there was a good correlation between the intensity of the preedge peak and the coordination number of the 1.64-Å shell. For this calcined sample, the proportion of Cr^{VI} is ca. 20% of the total chromium.

Hydrogenation at 250 °C for 2 h caused a further color change to gray-green, and the Cr K-edge EXAFS data showed that the Cr^{VI}O$_4$ centers had been lost with regeneration of a mean chromium environment similar to that of the pillared bentonite sample. This sample catalyzed the conversion of methanol to hydrocarbons and some oxygenates.

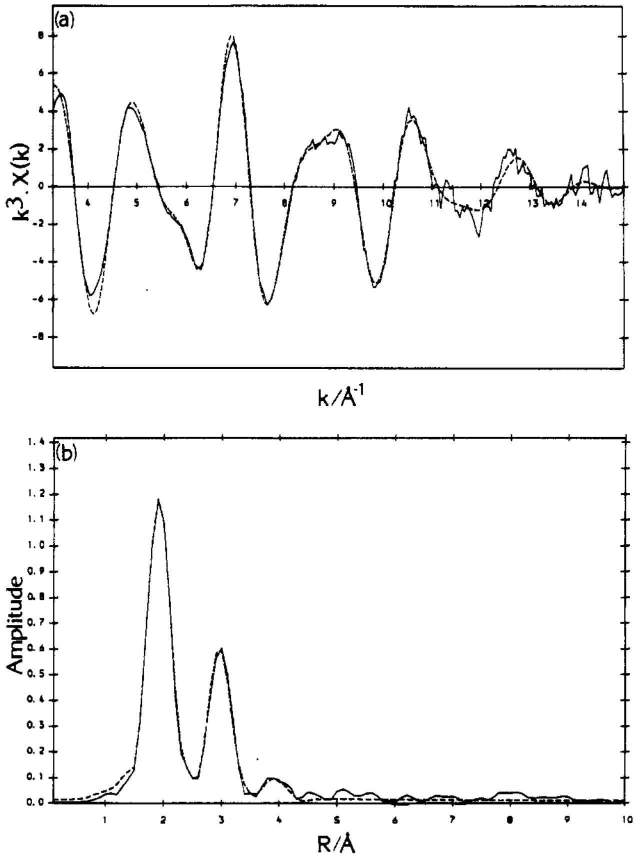

Figure 3. Cr K-edge EXAFS data of the chromium ion exchanged bentonite at room temperature and calcined at 250 °C: (a) k^3-weighted EXAFS and (b) the Fourier transform, phase-shift corrected for oxygen. Key: (—) experiment and (--) spherical wave theory for one O at 1.64 Å, five O at 1.95 Å, two Cr at 2.93 Å, and one Cr at 3.87 Å gives a fit with $R = 15\%$.

These results demonstrate that the cis-linked octahedral units formed in aqueous solution on hydrolysis of Cr^{III} solutions are retained on incorporation into a clay and are partially oxidized to a mixed-valence Cr^{VI}Cr^{III} material on calcination, with hydrogenation regenerating the octahedral CrO$_6$ units in the "chromia pillared clay" catalysts. This last material may have differing OH$_2$/OH$^-$ ligand sets as compared to the original ion-exchanged clay.

We are continuing our work to correlate the structural and catalytic properties of these materials.

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Crystal and Molecular Structures and Spectroscopic Properties of Au$_2$(tmb)Cl$_2$ (tmb = 2,5-Dimethyl-2,5-diisocyanohexane). Evidence for Quasi-One-Dimensional Linear Chains with Weak Au(I)···Au(I) Interactions in the Solid State

Quasi-one-dimensional (1D) metal complexes have been investigated extensively, as they exhibit a variety of low-dimensional phenomena. The square-planar transition-metal complexes of Rh(I), Ir(I), Pd(II), Pt(II), and Au(III)[1] and halogen-bridged mixed-valence metal complexes[2] are common monomeric units building these extended linear chains in the solid state. To our knowledge, there is no example of a 1D material in which Au(I) metal forms a linear chain without halogen bridging units. We now wish to report the synthesis, crystal and molecular structures, and spectroscopic characterization of $Au_2(tmb)Cl_2$ (tmb = 2,5-dimethyl-2,5-diisocyanohexane) in the solid state, which appears to be the first example of a multi-1D Au(I) network. This luminescent organometallic Au compound exhibits weak intermolecular Au···Au interactions in the solid state, which are detected by Raman spectroscopy and confirmed by interatomic Au···Au distances obtained by single-crystal X-ray data.

The stoichiometric reactions of $H[AuCl_4]$[3a] with tmb[3b] produce $Au_2(tmb)Cl_2$.[4] Suitable single crystals for X-ray diffraction studies[5] were obtained from slow evaporation of acetonitrile solutions. The molecular structure (Figure 1) exhibits a tmb ligand that bridges two Au atoms in the anti configuration and trans to Cl^- with no intramolecular Au_2 interactions. The Au–Cl distances (2.245 (7) and 2.247 (7) Å) are slightly shorter than those for $[AuCl_4]^-$ (2.28 Å),[6] $Au_2(dppm)Cl_2$ (dppm = $(Ph_2P)_2CH_2$; 2.288 (1) Å),[7a] and Ph_3PAuCl (2.279 (3) Å.[7b] Similarly, the Au–C distances (1.914 (21)–1.921 (22) Å) are also shorter than those for Au(MeNC)(CN) (1.98 (5) Å)[8] and $Au_2(dmb)(CN)_2$ (dmb = 1,8-diisocyano-*p*-menthane; 1.96–1.98 (1) Å).[9] The C≡N (1.14 (3) Å) and other C–C and C–H bond distances are all normal. Finally, there is no major deviation from the ideal 180° 2-coordination geometry around the Au atom and C≡N groups.

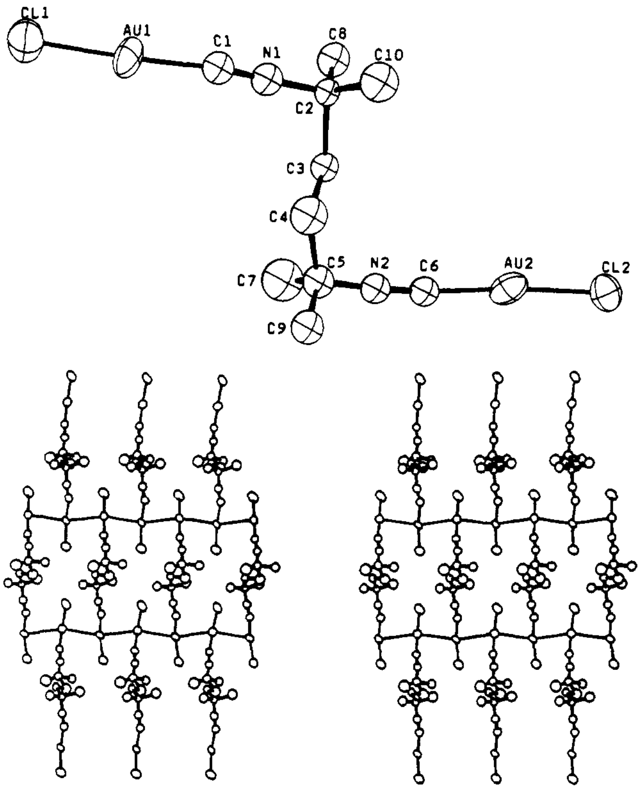

Figure 1. Top: Molecular structure of $Au_2(tmb)Cl_2$, showing 50% probability thermal ellipsoids. For clarity, the hydrogen atoms have been omitted. Bottom: Stereoview of the crystal packing.

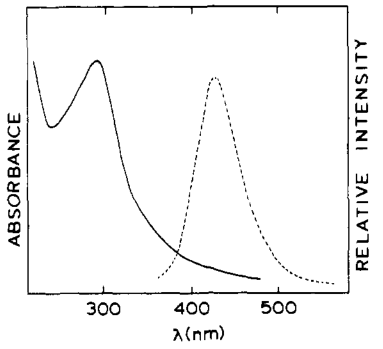

Figure 2. Solid-state UV–visible (—) and emission (---) spectra of $Au_2(tmb)Cl_2$ in KBr pellets.

The ^1H NMR spectra of $Au_2(tmb)Cl_2$ in CD_3CN solutions exhibit a temperature dependence of δ for the methyl (singlet; $\delta(-CH_3) = -3.292 \times 10^{-3}T$ (K) + 3.135; $\sigma = 0.999$) and methylene groups (unresolved multiplet; $\delta(-CH_2-) = 5.733 \times 10^{-4}T$ (K) + 1.378; $\sigma = 0.999$) between 243 and 323 K, suggesting the presence of an equilibrium between the anti and syn conformers. In the anti form, the methyl protons lie in the deshielding region due to the circulation of π electrons in the triple bond of the diisocyanide groups. The variation of $\delta(-CH_3)$ vs T (K) indicates that the concomitant increase in $\delta(-CH_3)$ with the reduction in T (K) is associated with a shift of the anti–syn equilibrium toward the anti conformation.

The description of the molecular packing in the crystal reveals multi-1D intermolecular nonbonding Au···Au contacts (r(Au···Au) = 3.3063 (3) Å); they appear as an infinite number of parallel Au atom chains interconnected by tmb ligands in an alternating fashion (left chain, right chain). This Au···Au separation is an intermediate value between the intermolecular Au···Au distances in solid $K[Au(CN)_2]$ (3.64 Å)[10] and Au(MeNC)(CN) (3.52–3.72

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(4) $Au_2(tmb)Cl_2$ was synthesized as follows. A 0.30-mmol amount of $H[AuCl_4]$ was stirred with an equivalent amount of tmb in boiling methanol (Aldrich Chemical Co.) for 1 h. Upon cooling, a pale yellow solid settled, which was washed with cold methanol (60 mg; isolated yield 32%). Anal. Calcd for $Au_2Cl_2C_{10}H_{16}N_2$: C, 19.09; H, 2.56; N, 4.95; Cl, 11.07. Found: C, 19.35; H, 2.38; N, 4.13; Cl, 10.83. Ir (KBr): 2980 m, 2936 w, 2239 vs (ν(C≡N)), 1469 m, 1454 m, 1393 m, 1371 m, 1319m, 1266 m, 1220 m, 1155 m, 1120 cm^{-1} m. The complex is soluble in CH_3CN and only slightly soluble in most polar organic solvents. The solid is an insulator with a resistivity larger than 10^7 Ω.

(5) Crystallographic data for $[Au_2(tmb)Cl_2]$ at 293 K: clear crystal of dimensions 0.4 × 0.4 × 0.2 mm; M_r = 629.08; orthorhombic; a = 12.5898 (12), b = 19.2179 (11), c = 6.5452 (3) Å; V = 1583.6 (2) $Å^3$; space group $Pna2_1$ (cell transformed from its original setting $P2_1nb$); Z = 4; D_c = 2.639 g cm^{-3}; μ(Mo Kα) = 187.75 cm^{-1}. Data were measured on an Enraf-Nonius CAD-4 diffractometer using Mo Kα radiation (λ = 0.71073 Å) (graphite monochromated) at a constant speed at 2.7°/min ($\omega/2\theta$ scan), with $2\theta \leq 44.8°$, *hkl* range 0–6, 0–13, and 0–20, respectively, and 1125 unique measured reflections. A linear absorption correction was applied with minimum and maximum transmission factors of 0.031 194 and 0.465 15, respectively. The structure was solved by direct methods by using the NRCVAX system[5b] with atomic scattering factors from Cromer and Waber.[5c] The convergence of the refinement process was achieved only with the $Pna2_1$ space group, *Pnam* leading to highly distorded geometries. The low scattering contribution of C and N compared to the two Au and Cl atoms prevents the anisotropic refinement of the tmb ligand, giving unrealistic thermal parameters. The H atoms positions were all calculated but not refined. At convergence, the final residuals were R = 0.040 and R_w = 0.036 for 937 independent observed reflections [$I_{net} \geq 2.5\sigma(I_{net})$]. The poor quality of the crystal combined with the spherical absorption correction is assumed to be responsible for the high goodness of fit. The tmb ligand binds two Au atoms in a pseudoanti fashion. The sequence of atoms joining Au(1) and Au(2) is quasiplanar. (b) Gabe, E. J.; Lee, F. L.; Le Page, Y. The NRCVAX Crystal Structure System. In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Databases*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Clarendon Press: Oxford, England, 1985; pp 167–174. (c) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*, Vol. IV, Ibers, J. A., Hamilton, W. C., Eds.; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B, pp 99–101 (present distributor Kluwer Academic Publisher, Dordrecht, The Netherlands).

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(4) Å),[8] the intramolecular Au···Au distance in $Au_2(dmb)(CN)_2$ (3.536 Å),[9] the van der Waals contacts (3.4 Å)[11] and the typical $r(Au_2)$ values (2.76–3.10 Å) for Au(I) dimers[12-16] and aggregates,[17] and the interatomic distance in Au metal (2.884 Å).[18] The value of the Au_3 angle is 163.66 (4)° and is similar to that reported for the polymeric 1D $AuTl(MTP)_2$ (MTP = $Ph_2P(CH_2)S$),[19] where the Au–Tl–Au′ and Tl–Au–Tl′ angles are 162.7 (1) and 162.9 (1)°, respectively. The solid $Au_2(tmb)Cl_2$ appears to be the first example of a 1D Au(I) material without halogen-bridging units.

The solid-state UV–visible spectra exhibit an absorption at 292 nm for $Au_2(tmb)Cl_2$ in KBr pellets.[20] In solution, this band is also observed $\lambda_{max} = 272$ nm, suggesting that this low-energy band does not arise from Au···Au interactions; a metal-centered d → p assignment is preferred.[20b] The solid-state luminescence spectrum (Figure 2) exhibits a maximum at 417 nm ($\tau_e = 0.70 \pm 0.03$ μs).[21] This excited-state energy (~2.9 eV) correlates well with those reported for solid $K[Au(CN)_2]$ (~3.1 eV at 78 K),[10b] solid $Au_2(dmb)(CN)_2$ (~2.8 eV at 293 K),[9] and some Au_2 compounds in solution.[22] The long lifetime and large separation between absorption and emission peaks (~10400 cm^{-1}) indicate that the luminescence is phosphorescence.

The solid-state vibrational spectra were also obtained in the 30–450-cm^{-1} range (ν(Au–Cl) = 352 (IR), 359 cm^{-1} (R); ν(Au–C) = 417 (IR), 390 cm^{-1} (R)). The intense Raman active intermolecular ν(Au···Au) mode is found in the lattice vibration region at 50 cm^{-1}.[23] The associated force constant, F(Au···Au), is 0.15 mdyn Å^{-1}. From an empirical equation relating r(M···M) and F(M···M) for the 5d elements ($r(M\cdots M) = 2.01 + 1.31 \times \exp(-F/2.36)$),[26] a 3.24-Å value for r(Au···Au) was obtained, which compares reasonably well with the observed r(Au···Au) of 3.31 Å (~2% difference). The only other reported $\nu(Au_2)$ value for nonbonded Au_2 compounds was located at 64 cm^{-1} [24] for $Au_2(ylid)_2$ (ylid = $Ph_2P(CH_2)_2^-$),[25] for which the intramolecular Au···Au separation is ~3.0 Å.[25] Other low frequencies have been observed in other weakly interacting M_2 complexes; $\nu(Rh)_2 = 60$ cm^{-1} [27a] and $r(Rh_2) = 3.193$ Å[27b] for $[Rh(CNPh)_4]_2^{2+}$.

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Supplementary Material Available: Tables of atomic positional parameters, bond distances, bond angles, anisotropic thermal parameters, and data collection parameters for $Au_2(tmb)Cl_2$ (4 pages); a table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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(20) (a) The UV–visible spectra in CH_3CN solutions exhibit three maxima at 196 (63200), 232 (19000) and 274 nm (5110 M^{-1} cm^{-1}) and a shoulder at 216 nm (~15000 M^{-1} cm^{-1}). The absorption spectrum of solid $Au_2(tmb)Cl_2$ is the same in NaCl, KBr, and CsI pellets. (b) This assignment is consistent with that for the $M(PPh_3)_3$ complexes (M = Pd(0), Pt(0)): Caspar, J. V. *J. Am. Chem. Soc.* **1985**, *107*, 6718. Recent SCF–Xα–SW molecular orbital calculations have suggested that substantial mixing of the d_{z^2} orbital with the s orbital occurs during the formation of the $d\sigma^*$ molecular orbital in the $[Au_2(H_2PCH_2PH_2)_2]^{2+}$ compound.[22] Although there is no experimental evidence for d_{z^2}–s–p_z orbital mixing in the mononuclear d^{10} complexes, the possibility of such a situation occurring remains. In solid $Au_2(tmb)Cl_2$, the intermolecular Au···Au distances are too large (~3.3 Å) to observe significant Au_n interactions forming bonding and antibonding molecular orbitals. The electronic absorption spectra in the solid state are not so different from those in solution. The metal-centered d → p assignment is preferred.

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Synthesis and Photochemical Reactions of a Layered Manganese Carbonyl–Zirconium Hydrogen Phosphate Compound

A large number of organometallic guest molecules have been intercalated into inorganic layered and zeolitic host lattices.[1,3] In the case of layered hosts, the layers separate to accommodate the guest, giving a material with alternating organometallic and inorganic layers. The most common reactions used to promote this intercalation are redox and ion exchange processes.[1,2] A Brønsted acid/base reaction has also been used to promote intercalation of organometallics, but has been restricted to substituted ferrocenes.[3] This communication reports the intercalation of an amine-substituted organometallic carbonyl complex into the acidic layered host α-$Zr(HPO_4)_2\cdot H_2O$, ZrP. Photolysis of this intercalated metal carbonyl leads to a surface-supported organometallic complex.

The dimeric manganese tricarbonyl complex $[(CO)_3Mn(\eta^5\text{-}C_5H_3(CH_3)CH_2\text{-})]_2NH$, Mn_2-NH, was prepared by first for-

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