At scan rates above 10 V s^{-1}, the waves complementary to those for oxidation at 1.1 V, and the reduction at -0.06 V, appear. By application of the method of Nicholson and Shain,[6] the specific rates for the S to O isomerization of the metastable 3+ species and the O to S isomerization of the metastable reduced species were determined as $(5.0 \pm 0.5) \times 10$ s^{-1} and $(2.0 \pm 0.2) \times 10$ s^{-1}, respectively. At low scan rates, <20 mV s^{-1}, the reduction wave at $E_{pc} = -0.06$ V decreases in amplitude, as is seen by comparing Figure 1c with Figure 1b. Intramolecular electron transfer can cause such a decrease, but other processes, for example, intermolecular electron transfer and loss of the electroactive species from the diffusion layer, can also contribute, so that, in the absence[7] of a more complete study, we can only set the upper limit, 4.1×10^{-2} s^{-1}, on the rate of intramolecular electron transfer.

The intervalence band for the stable form of the mixed-valence species, [S^{3+}/(SO)$^{2+}$], measured in acetone, has a maximum at $\sim$640 nm with $\epsilon \sim 4 \times 10$ M^{-1} cm^{-1}. The shift to high energies, as compared to substitutionally symmetric species, is a reflection of the difference in the redox potentials for the two sites. There is a second much stronger absorption at 452 nm which we attribute to ligand to metal charge transfer at Ru(III).[8]

The more usual redox couples conform to the Marcus relationship,[9] a necessary condition for its validity being that the distortions that bring energy matching at the two sites are nearly harmonic. Those in which the potential profile for at least one oxidation state has two minima—in our case, this is true in both oxidation states—comprise an important class which has not been investigated systematically. Devices of the kind we have described provide a means of studying electron transfer for them in the intramolecular mode. They may also provide a means of locking in charge transfer brought about by light absorption and, as such, may find application in high-density storage of memory. The excited state [S^{2+}/(SO)$^{3+}$]* which arises on absorption of light at $\sim$640 nm is expected to be quenched rapidly, and if intramolecular electron transfer is slow enough, isomerization to [S^{2+}/(OS)$^{3+}$] will occur.

Many examples of geometrical isomerization accompanying a change in oxidation states have been reported,[10] particularly by Bond and co-workers.[11] The appearance of linkage isomerizations, which depends on a change in back-bonding capacity attending a change in oxidation state, is predictable for many yet untested systems with a reasonable degree of certainty. The field has been greatly extended in the study of molecules in which the metal ion is bound by η^2 to organic ligands,[12] including aromatic molecules, and additional chromophores can easily be built into mixed-valence molecules. It needs to be acknowledged that there is precedent for the "double square" potential diagram featured in Figure 2.[13] The system that we describe is to be regarded as a prototype of others which can be devised to show "molecular hysteresis" and to our knowledge is the first to be deliberately synthesized to exhibit this behavior.

(6) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.
(7) Work on this system was interrupted by Sano's return to Nagoya University and will be continued there.
(8) For [(NH$_3$)$_5$RuS(CH$_3$)$_2$]$^{3+}$, this band appears at 453 nm. Stein, C. A.; Taube, H. *Inorg. Chem.* **1979**, *18*, 1168.
(9) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.
(10) Copious reference to earlier literature is made in the following: Gaudiello, J. G.; Wright, T. C.; Jones, R. A.; Bard, A. J. *J. Am. Chem. Soc.* **1985**, *107*, 888.
(11) See, for example: Bond, A. M.; Hambley, T. W.; Mann, D. R.; Snow, M. R. *Inorg. Chem.* **1987**, *26*, 2257.
(12) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 2439. Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 5403. Harman, W. D.; Wishart, J. F.; Taube, H. *Inorg. Chem.* **1989**, *28*, 2411.
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Preparation and Characterization of Layered Lead Halide Compounds[†]

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Recent reports of a very strongly bound exciton in the excited state of the layered perovskite-type compounds (RNH$_3$)$_2$PbI$_4$ (R = nonyl, decyl, ...)[1,2] renewed our interest in lead halide compounds, since significant third-order optical nonlinearity is often associated with such exciton-exhibiting materials.[3] During studies of the chemistry and optical properties of this and related compounds, we have discovered a novel series of layered lead halo compounds having related excited-state features, some of which are described herein.

Evaporating acetone, tetrahydrofuran (THF), or dimethylformamide (DMF) solutions of PbI$_2$ and RNH$_3$I (R = nonyl, decyl) provided thin films[4] of the reported compounds (RNH$_3$)$_2$PbI$_4$ having a strong, sharp absorption feature at 511 nm, consistent with the value of 2.44 eV (508 nm) reported for the exciton transition.[1] Pump–probe experiments[5] at ambient temperature showed that the exciton transition in films[4] of the decylammonium compound can be bleached efficiently, which means there exists a large resonant third-order optical nonlinearity. In the low-power regime, the bleaching efficiency, expressed as $\Delta a/Ia_0$ where a_0 is the ground-state absorption coefficient, Δa is the laser-induced absorption change, and I is the laser intensity, is 1.5×10^{-7} cm^2/W at 510 nm. This is a relatively large value but somewhat less than that observed for small CdS clusters.[5] Transient absorption limits the maximal bleachable exciton absorption to $\sim$27%.[6]

We hoped to find closely related compounds that retain the sharp "exciton" absorption feature but shifted to significantly lower energies. Incremental changes in chain length of the alkylammonium cation have little effect on the room temperature absorption feature of orange-colored (RNH$_3$)$_2$PbI$_4$.[1] However, use of methylammonium cation provides the very darkly colored compound (MeNH$_3$)PbI$_3$ in the cubic perovskite phase[7,8] (see Figure 1a), and we began to suspect that the cubic perovskite (MeNH$_3$)PbI$_3$ and the layered perovskite (RNH$_3$)$_2$PbI$_4$ (Figure 1b) are actually two extremes of a hitherto unknown structural series (RNH$_3$)$_2$(MeNH$_3$)$_{n-1}$Pb$_n$I$_{3n+1}$ (Figure 1). Here $n = \infty$ corresponds to the cubic perovskite compound (MeNH$_3$)PbI$_3$[7] (Figure 1a) and $n = 2, 3, ...$ ("bilayer", Figure 1c, "trilayer", ...) describe structures not previously known for any organic amine–metal halide systems.[9]

[†] Contribution No. 5582.
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(3) For PbI$_2$ itself, see, e.g.: Ishihara, T.; Goto, T. *Springer Proc. Phys.* **1988**, *36*, 72–75.
(4) Films of better optical quality result from adding poly(methyl methacrylate) (PMMA).
(5) Wang, Y.; Suna, A.; McHugh, J.; Hilinski, E. F.; Lucas, P. A.; Johnson, R. D. *J. Chem. Phys.* **1990**, *92*, 6927–6939.
(6) Possible origins of the transient absorption include monoexciton-biexciton transitions, see: Brodin, M. S.; Kadan, V. N.; Matsko, M. G. *Fiz. Tverd. Tela (Leningrad)* **1989**, *31*, 216–224.
(7) Weber, D. *Z. Naturforsch.* **1978**, *B33*, 1443–1445. Møller, C. K. *Nature* **1958**, *182*, 1436. Haupt, H. J.; Heidrich, K.; Künzel, H.; Maurersberger, P. *Z. Phys. Chem. (Munich)* **1978**, *110*, 63–73.
(8) When moisture is present, PbI$_2$ and MeNH$_3$I can form crystalline (MeNH$_3$)$_4$PbI$_6$·2H$_2$O: Vincent, B. R.; Robertson, K. N.; Cameron, T. S.; Knop, O. *Can. J. Chem.* **1987**, *65*, 1042–1046.

Communications to the Editor

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We found that evaporating solutions of the "bilayer" composition $(Me(CH_2)_8NH_3)_2(MeNH_3)Pb_2I_7$ provided bright red films with a strong, sharp absorption feature at 562 nm (2.21 eV). The bleaching efficiency of the exciton absorption in films[4] of the decylammonium analogue is 7.5×10^{-8} cm²/W at 570 nm, and a large transient absorption is again observed. We have not succeeded in growing single crystals of $(RNH_3)_2(MeNH_3)Pb_2I_7$ (R = nonyl, decyl) large enough for X-ray data collection, although powder samples of the nonyl compound have an X-ray diffraction pattern consistent with a layered structure, spacing 25.6 Å. However, from THF/ether solutions both (Ph-$(CH_2)_2NH_3)_2PbI_4$ (1) and $(Ph(CH_2)_2NH_3)_2(MeNH_3)Pb_2I_7$ (2) form marginally satisfactory single crystals, and their structures have been determined[10] (Figure 2a,b). The structure determinations reveal disorder and/or unresolved superlattice structure in the relative orientations of the lead–iodo octahedra.[2,11] In the resulting averaged structure of compound 1, both the phenylethylammonium ions and the bridging iodide ions are disordered across mirror planes, corresponding to a superposition of octahedra each twisted ca. 13.6° from tetragonal positions. In compound 2 the major component consists of octahedra each twisted ca. 12.1° from tetragonal positions; extra iodide ions I' with 10% occupancy have also been refined (see supplemenary material). In addition, the organic cations of compound 2 are very poorly located, again the result of disorder and/or large thermal motion. Nevertheless, the structure determinations (Figure 2a,b) unambiguously confirm the "monolayer" and "bilayer" assignments for compounds 1 and 2, respectively.

Layered structures have also been obtained for bromo and chloro compounds. Powders of nominal composition [Me-$(CH_2)_8NH_3]_2(MeNH_3)_{n-1}Pb_nBr_{3n+1}$ have been prepared having X-ray diffraction patterns consistent with "monolayer" (n = 1), "bilayer" (n = 2), and "trilayer" (n = 3) structures (layer spacings 22.6, 28.3, and 34.2 Å, respectively). Films of the monolayer composition have a sharp "excitonic" absorption maximum at 393 nm. Films of the bilayer and trilayer compositions have dominant absorption maxima at 430 and 450 nm, respectively, but also have weaker peaks at 390 and 530 nm, owing to imperfect "self-assembly" and the resulting presence of some of the monolayer and cubic $(MeNH_3)PbBr_3$[7] phases. The compound (Ph-$(CH_2)_2NH_3)_2PbBr_4$ has been obtained (layer spacing 16.7 Å), but we have not succeeded in preparing higher layered bromo compounds using phenethylammonium and methylammonium cations. The chloro compounds $(Me(CH_2)_8NH_3)_2PbCl_4$ and $(Ph(CH_2)_2NH_3)_2PbCl_4$ have been prepared (respective layer spacing 23.5 and 16.9 Å) having "excitonic" absorption at 330 nm, but attempts to prepare higher layered chloro phases have so far been unsuccessful.

The formation of these multilayer structures results from the different sizes of the alkylammonium ions. Methylammonium

(9) Monolayered perovskite-type compounds $(RNH_3)_2MX_4$ are well-known for, e.g., M = Cd, Cu, Mn, X = Cl; see: Steurer, W.; Depmeier, W. *Acta Crystallogr.* **1989**, *B45*, 555–562. Willett, R.; Place, H.; Middleton, M. *J. Am. Chem. Soc.* **1988**, *110*, 8639–8650 and references therein. Inorganic compounds with multilayered perovskite-type structures are also well-known, e.g., K_2NiF_4, $K_3Ni_2F_7$, $KNiF_3$ (Babel, D.; Herdtweck, E. *Z. Anorg. Allg. Chem.* **1982**, *487*, 75–84. Knox, K. *Acta Crystallogr.* **1961**, *14*, 583–585. Kijima, N.; Tanaka, K.; Marumo, F. *Acta Crystallogr.* **1983**, *B39*, 557–561), and certain layered metal oxo compounds, for instance, $MCa_2Na_{n-3}Nb_nO_{3n+1}$ and copper oxide superconductors (Treacy, M. M. J.; Rice, S. B.; Jacobson, A. J.; Lewandowski, J. T. *Chem. Mater.* **1990**, *2*, 279–286. Zhou, W. *Adv. Mater.* **1990**, *2*, 94–97. Sleight, A. W. *Science* **1988**, *242*, 1519–1527).

(10) For $(C_6H_5CH_2CH_2NH_3)_2PbI_4$, compound 1: space group $C2/m$, a = 32.508 (5) Å, b = 6.131 (1) Å, c = 6.185 (1) Å, β = 93.80 (1)°, temperature = −70 °C, R = 3.6%, R_w = 3.7% for 103 variables (all non-hydrogen atoms refined anisotropically) on 1606 unique reflections with $I > 3\sigma(I)$. Anal. C, H, N. For $(C_6H_5CH_2CH_2NH_3)_2(CH_3NH_3)Pb_2I_7$, compound 2: space group $P\bar{1}$, a = 8.794 (1) Å, b = 8.792 (1) Å, c = 22.766 (2) Å, α = 94.02 (1)°, β = 97.02 (1)°, γ = 90.18 (1)°, temperature = 21 °C, R = 5.9%, R_w = 6.3% for 182 variables (Pb and I refined anisotropically; C, N, and I' refined isotropically) on 3780 unique reflections with $I > 3\sigma(I)$. Anal. C, H, N. Full details of both structures are available as supplementary material.

(11) "Tilting" and other deviations from tetragonal or cubic symmetry are very common for structures consisting of corner-shared octahedra, as, for example, $MPbX_3$ itself;[7] see also, e.g.: Hutton, J.; Nelmes, R. J.; Meyer, G. M.; Eiriksson, V. R. *J. Phys. C* **1979**, *12*, 5393–5410 and references therein.
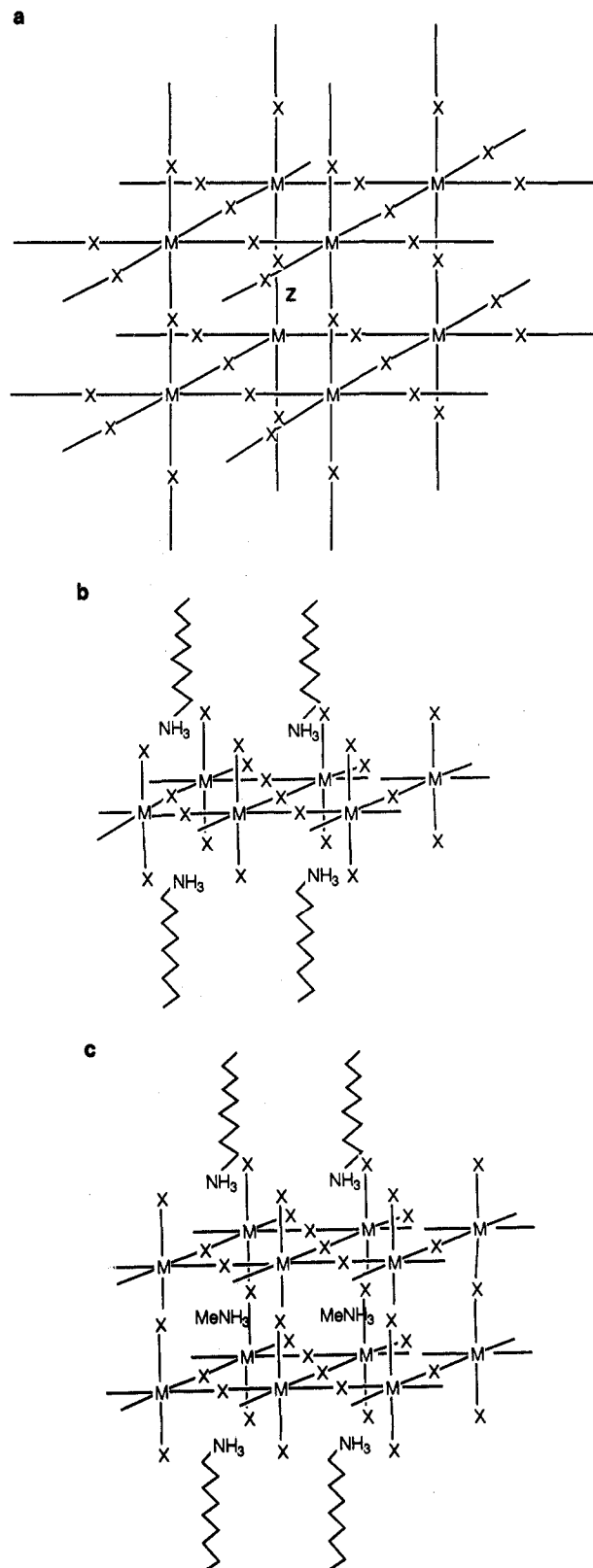

Figure 1. Representations of series of "layered perovskite-type" halo–lead compounds. (a) Cubic perovskite structure (M = Pb; Z = Cs, $MeNH_3$). (b) "Monolayer" (M = Pb). (c) "Bilayer" (M = Pb).

fits in the center of eight PbX_n corner-shared octahedra (the A site of the perovskite formula ABX_3) while phenethylammonium and long-chain alkylammonium ions fit only on the periphery of a set of four PbX_n octahedra. Thus the PbX_n framework adjusts itself, within limits, to accommodate the methylammonium and alkylammonium ions in the provided ratios. Another perspective, however, is that the long-chain alkylammonium ions "cap" the

a

b
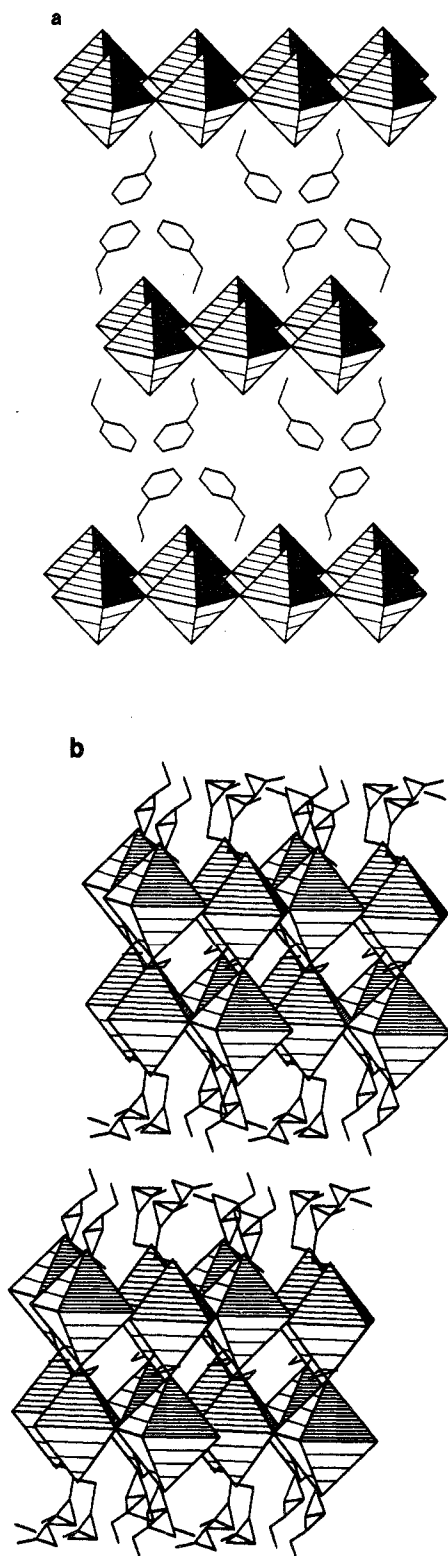
Figure 2. Representations of the layered structures $(C_6H_5CH_2CH_2NH_3)_2(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$. Only one set of disordered iodide ions is shown for each structure, and a single component of the disordered phenethylammonium cation is shown in Figure 2a. Selected distances (Å) and angles (deg) are given. (a) Compound **1**, $n = 1$, "monolayer": Pb–I$_{bridge}$, 3.158 (1), 3.178 (1); Pb–I$_{terminal}$, 3.204 (1); I$_{terminal}$–Pb–I$_{terminal}$, 180; I$_{bridge}$–Pb–I$_{bridge}$, 89.45 (3), 180; I$_{terminal}$–Pb–I$_{bridge}$, 88.65 (1), 90.91 (2); I$_{bridge}$–Pb–I′$_{bridge}$, 26.67 (4), 27.79 (3); Pb–I–Pb, 152.21 (4), 153.33 (4). (b) Compound **2**, $n = 2$, "bilayer": Pb–I$_{terminal}$, 3.130 (3), 3.138 (3); Pb–I$_{bridge,interplane}$, 3.263 (3), 3.272 (3); Pb–I$_{bridge,intraplane}$, 3.161 (2)–3.189 (2); I$_{terminal}$–Pb–I$_{interplane}$, 177.0 (1), 177.2 (1); I$_{terminal}$–Pb–I$_{intraplane}$, 89.07 (7)–93.86 (7); Pb–I$_{interplane}$–Pb, 180 (1); Pb–I$_{intraplane}$–Pb, 154.9 (1)–156.9 (1).

perovskite structure of $(MeNH_3)PbX_3$, providing a possible means of stabilizing colloidal "perovskite-type" lead halo complexes, which we will pursue elsewhere.

Developing Molecular Fischer–Tropsch Type Chemistry: The Triethylboron-Catalyzed Oligomerization of CO-Derived Methylene Groups from a (η^2-Formaldehyde)zirconocene Dimer

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The search for alternative routes to petrochemical products has remained a great challenge over the years. Investigations toward developing variations of the Fischer–Tropsch reaction for, e.g., selectively producing hydrocarbons from CO and hydrogen have been of great interest in this respect.[1] There is convincing evidence that the essential carbon–carbon coupling steps can be described as a chemistry of methylene units at the heterogeneous Fischer–Tropsch catalyst surface.[2] We have recently begun to develop the chemistry of homogeneous model systems which mimic some important aspects of this "CH$_2$-on-a-surface chemistry" using metallaoxirane complexes containing [Cp$_2$ZrOCH$_2$] units.[3] These molecular entities contain carbon monoxide derived CH$_2$ groups which often behave as methylene units being attached to a supporting metal oxide framework. We here report a novel reaction whereby these CO-derived methylene groups are catalytically removed from the metal oxide type carrier and oligomerized in a homogeneous system similar to what may be taking

(1) (a) E. L. Muetterties noted that "a so-called selective Fischer–Tropsch synthesis, an unknown element today (with the possible exception of polymethylene synthesis) but a desirable technological achievement, will be mechanistically differentiable from the Fischer–Tropsch synthesis and should receive a distinctive name when discovered". Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (b) For selected reviews, see: Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979**, *28*, 79. Rofer-De Poorter, C. K. *Chem. Rev.* **1981**, *81*, 441. Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61. Herrmann, W. A. *Angew. Chem.* **1982**, *94*, 118; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. See also: Henrici-Olivé, G.; Olivé, S. *Angew. Chem.* **1976**, *88*, 144; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136.

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