lous not only for the Nd, Sm, Ho, and Tm compounds, as indicated above, but also for ErCo₂, in which the magnetization diminishes with extreme abruptness near the Curie point (Figure 2). These phenomena are not understood in detail, but it is felt that they all stem from the variation of cobalt moment with the strength of the molecular field. In ErCo₂, for example, the abrupt decrease in magnetization near the Curie point is probably the cumulative effect of the normal decrease associated with the disappearance of the cooperative phase and the accompanying decrease of the moment associated with cobalt.

The first stage of the demagnetization in the Nd, Sm, and Ho compounds may be due to a collapse of the cobalt moment, brought on by the weakening of the molecular field. This is, however, quite speculative. The only thing which is clear in these cases is that the phenomena probably do not originate with impurities since similar effects were noted by Ross and Crangle[11] in their study of these compounds and by Walline and Wallace[27] in their investigation of NdNi and HoNi.

(27) R. E. Walline and W. E. Wallace, *J. Chem. Phys.*, **41**, 1587 (1964).

In YCo₂ and CeCo₂ the magnetic interactions involve only the cobalt component. The measured Co moment is 0.05 μ_B per atom, whereas, as noted above, when Co is in chemical union with a strongly magnetic partner, it carries a moment of 0.8 to 1.0 μ_B per atom. The low moment in YCo₂ is probably due to the nonmagnetic nature of Y, which means it supplies no field with which Co may couple. However, the Curie point of YCo₂ is surprisingly high compared with other members of the series, and the possibility cannot be excluded that it is ferrimagnetic or that it possesses some type of complicated magnetic structure.

The susceptibility of CeCo₂ rises rapidly with decreased temperature near 4°K. No evidence of a Curie point is obtained in measurements extending to 2°K., but it may become ferromagnetic at lower temperatures.

Platinum–Tin Metal Clusters

BY R. V. LINDSEY, JR., G. W. PARSHALL, AND U. G. STOLBERG

A complex anion, [Pt₃Sn₈Cl₂₀]⁻⁴, has been obtained by reaction of stannous chloride with PtCl₂ or with [Cl₂Pt(SnCl₃)₂]⁻² in acetone. Salts of this new anion react with 1,5-cyclooctadiene to give a neutral compound, (C₈H₁₂)₃Pt₃Sn₂Cl₆. Both the anion and the neutral complex are believed to be derivatives of a Pt₃Sn₂ metal cluster.

Stannous chloride and platinous chloride react in dilute hydrochloric acid to give bright red solutions which have found application in the colorimetric determination of platinum. Meyer and Ayres[1] found evidence for the presence of several platinum–tin complexes in these solutions. More recently, salts of the [Cl₂Pt(SnCl₃)₂]⁻² and [Pt(SnCl₃)₅]⁻³ anions have been isolated[2-4] from solutions of these chlorides in dilute hydrochloric acid and in methanol.

Examination of the products formed from SnCl₂ and PtCl₂ in acetone solution has now shown the existence of a third anionic complex, [Pt₃Sn₈Cl₂₀]⁻⁴. Salts of this species, in contrast to those of [Pt(SnCl₃)₅]⁻³, are stable to air and can be recrystallized from a number of solvents. Treatment of [Pt₃Sn₈Cl₂₀]⁻⁴ solutions with 1,5-cyclooctadiene gives a neutral compound, (C₈H₁₂)₃Pt₃Sn₂Cl₆.

(1) A. S. Meyer and G. H. Ayres, *J. Am. Chem. Soc.*, **77**, 2671 (1955).
(2) R. D. Cramer, E. L. Jenner, R. V. Lindsey, Jr., and U. G. Stolberg, *ibid.*, **85**, 1691 (1963).
(3) A. G. Davies, G. Wilkinson, and J. F. Young, *ibid.*, **85**, 1692 (1963).
(4) R. D. Cramer, R. V. Lindsey, Jr., C. T. Prewitt, and U. G. Stolberg, *ibid.* **87**, 658 (1965).

I   II
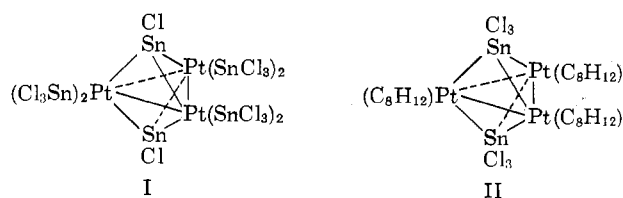
These complexes are formulated as derivatives of a Pt₃Sn₂ metal cluster, a trigonal bipyramid with platinum atoms in the equatorial plane and tin atoms at the apices. In the anionic complex I, two SnCl₃⁻ groups are coordinated to each platinum, while in the neutral complex II these are replaced by the chelating diolefin ligands. Support for this displacement is obtained from the infrared spectra. In [Pt₃Sn₈Cl₂₀]⁻⁴ salts, a very strong band appears at 330 cm.⁻¹, a frequency which is characteristic of σ-bonded SnCl₃⁻ groups in the mononuclear complexes.[5,6] This absorption is absent in the cyclooctadiene complex which has, instead, bands

(5) R. V. Lindsey, Jr., G. W. Parshall, and U. G. Stolberg, *ibid.*, **87**, 658 (1965).
(6) D. M. Adams and P. J. Chandler, *Chem. Ind.* (London), 269 (1965).

assignable to π-coordinated diene as in dichloro-1,5-cyclooctadieneplatinum. The proposed trigonal-bipyramidal structure is like that found in $(C_5H_5)_3Ni_3(CO)_2$[7] and in $[(C_6H_6)_3Co_3(CO)_2]^+$ in which three equatorial metal atoms bearing hydrocarbon ligands are bridged by apical CO groups.[8]

The formation of $[Pt_3Sn_8Cl_{20}]^{-4}$ from $PtCl_2$ and $SnCl_2$ or, alternatively, from $[Cl_2Pt(SnCl_3)_2]^{-2}$ and $SnCl_2$ is interesting in that the platinum atoms are apparently reduced to the zerovalent state. Stannous chloride must be the reducing agent since $[SnCl_6]^{-2}$ salts are isolated in roughly stoichiometric amounts according to the equation

$$3PtCl_2 + 11SnCl_2 + 10Cl^- \longrightarrow [Pt_3Sn_8Cl_{20}]^{-4} + 3[SnCl_6]^{-2}$$
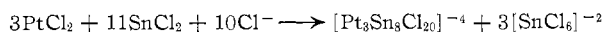
A similar oxidation–reduction reaction was noted previously by Meyer and Ayres[1] in the reduction of K_2PtCl_4 with excess $SnCl_2$ in hydrochloric acid solution. Hydrolysis of the reaction mixture gave a brown precipitate formulated as a $[PtSn_4Cl_4]^{+4}$ salt and one mole of stannic ion per mole of platinum. We likewise find stoichiometric reduction of Pt^{+2} to Pt^0, but analysis of the precipitated complex suggests the composition $PtSn_3Cl_3 \cdot 6H_2O$. The complex probably is a trimer containing the Pt_3Sn_2 metal cluster since treatment with 1,5-cyclooctadiene gives the neutral compound II. It seems likely that the precipitated hydrolysis product is an analog of I in which the six peripheral tin ligands are partially hydrolyzed, e.g., $[ClSn(H_2O)_2]^+$ or $[ClSn(OH)(H_2O)]$.

Experimental Section

$[(CH_3)_4N]_4[Pt_3Sn_8Cl_{20}]$.—A concentrated acetone solution of 5.6 g. of $SnCl_2 \cdot 2H_2O$ was added to a solution of 11.0 g. of $[(CH_3)_4N]_2[Cl_2Pt(SnCl_3)_2]$ in 500 ml. of acetone. The mixture became red and, after about 30 sec., crystals began to precipitate. The mixture was stirred for 1 hr. and was filtered and washed with acetone. The dark red $[(CH_3)_4N]_4Pt_3Sn_8Cl_{20}$ was recrystallized by addition of acetone to a nitromethane solution. The solid gave no paramagnetic resonance signal.

Anal. Calcd. for $C_{16}H_{48}Cl_{20}N_4Pt_3Sn_8$: C, 7.57; H, 1.91; Cl, 27.9; N, 2.22; Pt, 23.1; Sn, 37.4. Found: C, 7.73; H, 2.19; Cl, 26.9; N, 1.95; Pt, 23.1; Sn, 35.7.

$[(C_2H_5)_4N]_4[Pt_3Sn_8Cl_{20}]$.—A mixture of 7.95 g. of platinum(II) chloride, 16.90 g. of tin(II) chloride dihydrate, and 100 ml. of acetone was stirred under nitrogen overnight. An exothermic reaction began immediately and persisted for about 1 hr. At the end of this time, the solution was deep red. Little change in appearance occurred subsequently. The mixture was filtered under nitrogen to remove unreacted $PtCl_2$. The filtrate was stirred with a solution of 12.5 g. of tetraethylammonium chloride in 40 ml. of methanol. A deep red solid precipitated. Prolonged extraction of this solid with acetone left a dark residue. Recrystallization of the residue from nitromethane gave 5 g. of white crystals with an X-ray powder pattern identical with that of authentic tetraethylammonium hexachlorostannate(IV).

On cooling or evaporation, the acetone extracts and the mother liquor deposited dark red, almost black, crystals. Recrystallization from acetone gave 8.5 g. of fine, red needles of $[(C_2H_5)_4N]_4Pt_3Sn_8Cl_{10} \cdot (CH_3)_2CO$; m.p. >250°.

Anal. Calcd. for $C_{35}H_{86}Cl_{20}N_4OPt_3Sn_8$: C, 14.89; H, 3.07;

Cl, 25.12; Pt, 20.73; Sn, 33.64. Found: C, 14.66; H, 3.24; Cl, 25.48; Pt, 20.82; Sn, 33.15.

The infrared spectrum showed a very strong Sn–Cl stretching band at 332 cm.$^{-1}$ with a shoulder at 304 cm.$^{-1}$. Less intense bands also appeared at 107, 123, and 470 cm.$^{-1}$. Solutions of $[(C_2H_5)_4N]_4Pt_3Sn_8Cl_{20}$ and of the $PtCl_2$–$SnCl_2$ mixture in acetone showed no paramagnetic shift of the solvent band in the proton magnetic resonance spectrum.

The conductance of a nitrobenzene solution of the tetraethylammonium salt was 47.0 (extrapolated to infinite dilution).[9]

(1,5-cyclooctadiene)$_3Pt_3Sn_2Cl_6$.—Treatment of an acetone solution of $[(C_2H_5)_4N]_4Pt_3Sn_8Cl_{20}$ with excess of 1,5-cyclooctadiene in air gave a mixture of $[(C_2H_5)_4N]_2SnCl_6$ and an orange cyclooctadiene complex. Extraction of the mixture with hot dichloromethane gave an orange solution from which the cyclooctadiene complex was selectively precipitated by addition of nitromethane. The elemental analyses and the infrared spectrum showed the presence of nitromethane in the orange crystals obtained in this way. The X-ray diffraction pattern of a crystal (monoclinic, space group C_c or $C_{2/c}$) gave the unit cell constants: $a = 29.60, b = 10.43, c = 22.08$ Å.; $\beta = 96°\ 15'$; eight molecules per unit cell.

Anal. Calcd. for $C_{24}H_{36}Pt_3Sn_2Cl_6 \cdot CH_3NO_2$: C, 21.1; H, 2.77; Cl, 14.9; N, 0.99; Pt, 41.2; Sn, 16.7; mol. wt., 1421. Found: C, 21.9; H, 2.95; Cl, 13.6; N, 1.26; Pt, 41.0; Sn, 15.2; mol. wt., 1380 (X-ray).

Two recrystallizations from dichloromethane gave red-orange cubes of $(C_8H_{12})_3Pt_3Sn_2Cl_6$.

Anal. Calcd. for $C_{24}H_{36}Cl_6Pt_3Sn_2$: C, 21.19; H, 2.67; Cl, 15.64; Pt, 43.05; Sn, 17.45; mol. wt., 1360. Found: C, 21.25; H, 2.73; Cl, 15.62; Pt, 44.47; Sn, 16.18; mol. wt., 1200 (cryoscopically in C_6H_6).

The long wave length infrared spectrum showed Sn–Cl stretching bands at 309 (vs) and 322 (m) cm.$^{-1}$. Solutions in dichloromethane and in nitrobenzene were nonconductive.[9]

Identification of Cyclooctadiene.—A suspension of 0.57 g. of $(C_8H_{12})_3Pt_3Sn_2Cl_6$ in 20 ml. of dichloromethane was stirred with a solution of 2.6 g. of potassium cyanide in 5 ml. of water at 25° for 47 hr. The orange complex slowly dissolved and the mixture became colorless. Gas chromatography of the organic layer gave 138 mg. (102%) of 1,5-cyclooctadiene. The infrared spectrum and the gas chromatography retention times (silicone rubber and tris-β-cyanoethoxypropane columns) were identical with those of 1,5-cyclooctadiene.

Filtration of the aqueous layer gave a black solid, apparently platinum metal. On cooling, the filtrate gave 0.16 g. of off-white needles of $K_2Pt(CN)_4$ which was identified by comparison of the infrared spectrum with that of an authentic sample[10] (γ_{CN} 4.65, 4.68 μ).

Anal. Calcd. for $C_4K_2N_4Pt$: N, 14.9. Found: N, 15.1.

Hydrolysis of a K_2PtCl_4–$SnCl_2$ Mixture.—A dark red solution of 0.415 g. of K_2PtCl_4 and 0.45 g. of $SnCl_2 \cdot 2H_2O$ in 10 ml. of 1.185 M hydrochloric acid was titrated with 37 ml. of water. At this point, a brown solid precipitated and was isolated by centrifugation. The precipitate was washed with 0.25 M hydrochloric acid and was dried under vacuum to give a black, acetone-soluble solid. Emission spectroscopy indicated the presence of less than 0.1% potassium.

Anal. Calcd. for $PtSn_3Cl_3 \cdot 6H_2O$: Pt, 25.5; Sn, 46.6; Cl, 13.9. Found: Pt, 25.3; Sn, 46.5; Cl, 14.2.

Solutions of the black solid in acetone or 3 M hydrochloric acid reacted with tetraethylammonium chloride to give deep red solids. Treatment of a nitromethane solution of such a red solid with excess 1,5-cyclooctadiene gave orange crystals of $(C_8H_{12})_3Pt_3Sn_2Cl_6 \cdot CH_3NO_2$. The X-ray powder pattern was identical with that of crystals obtained from $[(C_2H_5)_4N]_3Pt_3Sn_8Cl_{20}$ and cyclooctadiene.

(7) A. A. Hock and O. S. Mills, "Advances in Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 640.
(8) (a) E. O. Fischer and O. Beckert, *Angew. Chem.*, **70**, 744 (1958); (b) P. Chini and R. Ercoli, *Gazz. chim. ital.*, **88**, 117 (1959).
(9) The authors are indebted to Dr. Y. T. Chia for these measurements.
(10) D. M. Sweeney, I. Nakagawa, S-I. Mizushima, and J. V. Quagliano, *J. Am. Chem. Soc.*, **78**, 889 (1956).