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Magnetic Properties of Intermetallic Compounds between the Lanthanides and Nickel or Cobalt[1]

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The magnetic properties of two groups of intermetallic compounds are reported—the $LnNi_2$ and the $LnCo_2$ series, where Ln represents Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, and Y. These compounds are all isostructural, having the $MgCu_2$ structure. $CeNi_2$ and YNi_2 exhibit only Pauli paramagnetism. $CeCo_2$ may have a Curie temperature below 2°K. All other compounds order magnetically with Curie temperatures ranging from 12°K. for $TmNi_2$ to 410°K. for $GdCo_2$. Except for nonmagnetic $CeNi_2$ and YNi_2 and for $SmNi_2$, where the multiplet spacing is comparable with kT, all compounds in the $LnNi_2$ series exhibited Curie–Weiss behavior in the paramagnetic region, with effective moments as expected of the free tripositive lanthanide ions. In the $LnCo_2$ series, however, the behavior in the paramagnetic region is more complex and in the main is yet to be clarified. Improved values for the moments of the compounds in the ferromagnetic state are presented and compared with available neutron diffraction results. Crystal field effects partially quench the orbital angular momentum of the lanthanide ions. However, the quenching is weaker in $LnNi_2$ than had been expected on the basis of considerations set forth by Bleaney so that the effects are only apparent in the ferromagnetic region and at 4°K. The quenching effects are stronger in the $LnNi_2$ than in the $LnCo_2$ series.

Introduction

This study forms a part of a continuing program in this laboratory dealing with the magnetic and structural features of intermetallic compounds in which one component is a lanthanide and the other is a transition metal of the first long period. Specifically, the present study is concerned with the series of compounds designated as $LnNi_2$ and $LnCo_2$ in which Ln represents Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, and Y. The characteristics of some of these compounds in the ferromagnetic state were described in earlier publications[3,4] from this laboratory. The present study is primarily concerned with their behavior in the paramagnetic region, but it also includes improved values for the moments in the ferromagnetic form obtained using considerably higher fields than were available in the earlier work.

In previous studies of these compounds[3,4] it was established that (1) Ni in the $LnNi_2$ compounds was nonmagnetic and (2) the Ln moment measured at 4.2°K., except for Gd, was much lower than that of the free tripositive ion. The reduced moment was attributed[3,5] to partial quenching of the orbital moment by the crystalline field. Bleaney[5] has estimated the splitting in the $LnNi_2$ series and concluded that in some cases they exceed kT_c, where T_c is the observed Curie temperature, indicating that exchange is weaker than the crystal field interaction. If Bleaney's estimates are correct, deviations from Curie–Weiss behavior should occur at low temperatures. For example, with $PrNi_2$ and $TmNi_2$, for which the ground state is a singlet, the Van Vleck temperature-independent paramagnetism should be observed before the sample begins to order magnetically. If so, the limiting susceptibility in these cases can be used to establish the magnitude of the crystal field splittings, following the classic technique of Penney and Schlapp.[6] This procedure can also be used to establish the splitting in other cases in which degenerate ground states are obtained—by detailed analysis of the deviations from Curie–Weiss behavior. The primary purpose of the present study was to ascertain whether the low temperature deviations from Curie–Weiss behavior expected from Bleaney's estimate of the crystal field splitting in the $LnNi_2$ compounds actually occurs, and, if so, to determine the splittings experimentally, for a quantitative comparison with Bleaney's theoretical estimate. The investigation was later broadened to include the $LnCo_2$ compounds, with particular emphasis on their paramagnetic behavior, concerning which there was no available information.

Experimental Section

Samples were prepared using techniques which are now standard[3,7,8] for these kinds of materials. Stoichiometric proportions of the component metals were fused together using levitation and/or high-purity magnorite crucibles, with subsequent annealing under high vacuum at 500 to 800° to suppress largely or to eliminate extraneous phases. The absence of impurity phases was established by X-ray diffraction techniques using a G.E. XRD-3 diffractometer equipped with a scintillation counter.

Susceptibility measurements were made from liquid helium temperature to room temperature using the Faraday method. Saturation moments were determined by this same technique at either 4.2 or 2°K. using applied fields up to 21 koersteds and extrapolating to infinite field. More complete descriptions of the procedures used in this laboratory have been published previously.[9,10]

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[1] This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

[2] From a dissertation submitted by John Farrell to the Graduate Faculty of the University of Pittsburgh in partial fulfillment of the requirements for the Ph.D. degree, 1964.

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Results and Discussion

The $LnNi_2$ Compounds.—A summary of the results obtained for these compounds is given in Table I. Since $LuNi_2$,[8] YNi_2, and $CeNi_2$ are Pauli paramagnets and since the moment of $GdNi_2$ is close to the moment of Gd^{3+}, it appears that Ni is nonmagnetic throughout the series and that Ce is in the quadrapositive, nonmagnetic state. Hence, for the remaining members of the series, the measured moments can be ascribed to their lanthanide component. Although the ferromagnetic moments are well above those reported previously,[3,4,11] Table I shows them to be lower than the moments of the respective free tripositive ions.[12] These lower moments, as stated previously, are apparently due to partial quenching of the orbital angular momentum by crystalline fields.

TABLE I

MAGNETIC PROPERTIES OF THE $LnNi_2$ COMPOUNDS

	Ferromagnetic results			Paramagnetic results		
Compd.	μ_{sat}[a] μ_B/formula unit	gJ μ_B/formula unit	T_c, °K.[b]	μ_{eff}	$g\sqrt{(J + 1)}$	θ, °K.[c]
YNi_2			Pauli paramagnet			
$CeNi_2$			Pauli paramagnet			
$PrNi_2$	0.86[d]	3.20	...[e]	3.57	3.58	4
$NdNi_2$	1.80	3.27	16	3.74	3.62	10
$SmNi_2$	0.25	0.71	21	...	...	...
$GdNi_2$	7.1	7.00	85	7.82	7.95	78
$TbNi_2$	7.8	9.00	45	9.82	9.72	35
$DyNi_2$	9.2	10.00	30	10.4	10.60	23
$HoNi_2$	8.4	10.00	22	10.5	10.60	12
$ErNi_2$	6.8	9.00	21	9.37	9.60	11
$TmNi_2$	3.20[d]	7.00	...[e]	7.28	7.60	0

[a] Obtained by extrapolation to infinite field, $T = 4.2$°K. except as indicated. [b] T_c = Curie temperature. [c] θ = Weiss constant. [d] This is not the saturation moment. It is the measured moment at 2°K. and 20 koersteds. [e] These compounds may not be ferromagnetic at 2°K. (see text).

All of the compounds in this series, except $SmNi_2$ and the Pauli paramagnets $CeNi_2$ and YNi_2, exhibited Curie–Weiss (C–W) behavior. The experimental effective moments, μ_{eff}, are in satisfactory agreement with the free ion values as indicated in Table I. Susceptibility–temperature results for $SmNi_2$ are given in Table II. The temperature dependence of the susceptibility of this compound closely resembles that of elemental Sm, as reported by Lock.[13] Undoubtedly, contribution of the first excited multiplet, $J = 7/2$, of Sm^{3+} is responsible for the observed dependence of susceptibility on temperature. The C–W behavior exhibited by the remaining compounds in this series confirms that the multiplet intervals are large compared to kT and, furthermore, shows that there is sufficient population of the excited crystal field levels at the higher temperatures so that deviations from C–W behavior are not observed.

TABLE II

MOLAR SUSCEPTIBILITIES (χ) OF $SmNi_2$ AND $CeCo_2$

	$10^3\chi$, e.m.u./mole	
Temp., °K.	$SmNi_2$	$CeCo_2$
4		5.98
10		4.12
20	38.6	3.23
40	3.10	2.76
60		2.33
80	1.72	2.23
120	1.42	
160	1.29	
200	1.22	
240	1.18	
280	1.15	

Earlier it was indicated that the prime concern in studying the paramagnetic behavior of the $LnNi_2$ compounds was with the details of the deviation from C–W behavior near the low-temperature limit of the paramagnetic region—to determine if there are deviations and, if so, to ascertain whether the form and extent of the deviations are in accord with that expected from Bleaney's estimates of the crystal field splittings. The analysis is inapplicable to the Y, Ce, and Gd compounds since the ion is in an S state and, hence, is immune to the interaction under consideration and to $SmNi_2$ owing to complications arising from the contribution of the $J = 7/2$ state. Of the remaining seven compounds $PrNi_2$ and $TmNi_2$ represent the most favorable cases for examination in that for them the splitting (as estimated by Bleaney) relative to the exchange interaction is greatest. The first crystal field excited states were estimated[5] to lie at $kT_e = 77$ and 37°K. for $PrNi_2$ and $TmNi_2$, respectively. For $PrNi_2$ a splitting of this magnitude would lead to a perceptible deviation from C–W behavior at about 60°K. and a strong positive deviation of about 70% at 15°K. A similar situation would obtain for $TmNi_2$ except that the deviation would first become noticeable at about 35°K. In each of these cases linearity of χ^{-1} *vs.* T persists to 15°K., indicating that the first excited state lies at $T_e = 15$°K. or below.

The magnetization–temperature behavior of the Tm and Pr compounds below 15°K. indicates a tendency toward saturation. This can be interpreted either as the beginning of the region of Van Vleck paramagnetism or as due to the onset of ferromagnetism. It appears that in these materials the crystal field and exchange interactions are comparable in magnitude, and, on the basis of bulk magnetic measurements, it is not possible to ascertain whether they are Van Vleck paramagnets or ferromagnets with moments substantially reduced by the quenching effect of the crystal field. Clarification of their behavior below 15°K. must await additional observations—neutron diffraction work, heat capacity studies, etc., which are currently under way. The other seven compounds show well-defined Curie temperatures and are regarded at present as ferromagnetic materials.

The results obtained for the $LnNi_2$ compounds in the ferromagnetic state show that, except for $GdNi_2$, the moment is well below that expected for the free tripositive ion. Thus, the new results obtained using

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(11) J. W. Ross and J. Crangle, *Phys. Rev.*, **133**, A509 (1964).

(12) The present result for $SmNi_2$ is lower. However, it has been established that the earlier result was erroneous in that the sample was very seriously contaminated with Gd.

(13) J. M. Lock, *Proc. Phys. Soc.* (London), **B70**, 566 (1957).

improved techniques reinforce the earlier conclusion[3,5] that the moment as measured at 4.2°K. is partially quenched by the crystal field. The present results make it clear that the crystal field interaction in this series of compounds is weaker than had been anticipated on the basis of Bleaney's considerations. They show that the interaction is so weak that it is without effect at the higher temperature where the paramagnetic form exists. In consequence, the Penney–Schlapp procedure cannot be used to establish the splitting. However, from the appreciable quenching of the ferromagnetic moments it can safely be inferred that the first excitation energy exceeds kT_e with $T_e = 4.2$°K. Thus, T_e must lie between 4 and 15°K. for Pr in $PrNi_2$ and the first excitation energy must be of comparable magnitude in the other nickel compounds.

The $LnCo_2$ Compounds.—A summary of the magnetic results for these compounds is given in Table III. The data for the Nd, Tb, Ho, and Er compounds in the ferromagnetic state are in good agreement with recent neutron diffraction results of Moon, Koehler, and Farrell,[14] but not with those of Ross and Crangle.[11] The latter used unannealed samples. This probably accounts for the discrepancy since it has been observed in this laboratory that the moment as measured is increased during the annealing process.

TABLE III

MAGNETIC PROPERTIES OF THE $LnCo_2$ COMPOUNDS

Compd.	μ_{sat}[a] μ_B/formula unit	T_c, °K.[b]	θ, °K.[c]
YCo_2	0.10	320	. . .
$CeCo_2$	. . .	. . .	. . .
$PrCo_2$	3.2	50	. . .
$NdCo_2$	3.8	116	107
$SmCo_2$	2.0	259	. . .
$GdCo_2$	4.9	. . .	. . .
$TbCo_2$	6.7	256	228
$DyCo_2$	7.6	159	129
$HoCo_2$	7.8	95	. . .
$ErCo_2$	7.0	36	28
$TmCo_2$	4.7	18	. . .

[a] Obtained by extrapolation to infinite field; $T = 4.2$°K. [b] T_c = Curie temperature. [c] θ = Weiss constant.

For the heavier lanthanide compounds, the results in the ferromagnetic state can be rather closely accounted for by assuming the fully free ion lanthanide moments coupled parallel to each other and antiparallel to Co moments of 1 μ_B/Co. This interpretation is consistent with the neutron diffraction data for the Tb, Ho, and Er[14] compounds as shown in Table IV. Significantly, both bulk magnetic and neutron diffraction measurements show that the Ln–Co coupling in $NdCo_2$ is not antiparallel, but parallel. In the Nd ion $J = L - S$, whereas in the heavier lanthanides $J = L + S$. Thus, there is antiparallel coupling between the lanthanide and cobalt spins in each of the $LnCo_2$ compounds, and the magnetic structure in this respect corresponds exactly with that noted earlier[15–17] for the closely related Haucke phases, the $LnCo_5$ compounds.

It is of interest to note that the magnetic structures of the $LnCo_2$ compounds are consistent with the behavior expected of them on the basis of present-day understanding of the magnetic interactions in such materials. Exchange in the elemental lanthanides involves primarily the Ruderman–Kittel–Yosida (RKY) interaction,[18,19] the oscillatory polarization of the conduction electrons. The e.s.r. work by Peter[20] and Jaccarino, *et al.*,[21,22] involving Gd and $GdAl_2$ has shown that there is negative or antiferromagnetic polarization of the conduction electrons at the Gd site; *i.e.*, the conduction electrons have at that point a net spin opposed to the spin vector of the Gd ion core. Spin resonance evidence for other lanthanides is not available, but it is generally assumed that they behave similarly. The n.m.r. work by Jaccarino, *et al.*, on the cubic Laves phase series $LnAl_2$ has shown[21] that the negative polarization of the conduction electron extends out to the Al site. Assuming (1) that the same situation obtains in the isomorphous $LnCo_2$ series and (2) that the Co-conduction electron-exchange interaction is ferromagnetic, as was observed for Fe and Fe-based alloys by Stearns[23] using the Mössbauer technique, one expects the cobalt moments to be coupled to the lanthanide moments ferromagnetically for a light, and antiferromagnetically for a heavy lanthanide. This is, as was pointed out above, the observed coupling pattern in the $LnCo_2$ compounds.

TABLE IV

COMPARISON OF NEUTRON DIFFRACTION AND MAGNETIC DATA

	Neutron diffraction data[a]			Magnetic data
Compd.	μ_B/Ln	μ_B/Co	μ_B/formula unit	μ_B/formula unit
$NdCo_2$	2.6	+0.8	4.2	3.8
$TbCo_2$	8.8	−1.0	6.8	6.7
$HoCo_2$	9.5	−1.0	7.5	7.8
$ErCo_2$	8.9	−1.0	6.9	7.0

[a] Results of Moon, *et al.*, ref. 14. Uncertainty in the moments is ±0.2μ_B.

The Curie temperatures are also consistent with this coupling mechanism. For exchange between the f shell spins *via* the conduction electrons the Curie temperatures are proportional to $(g - 1)^2J(J + 1)$ if the interaction is long range or to $S(S + 1)$ if the interaction is short range.[24,25] The best fit for the data is found for a long-range interaction as shown in Figure 1. The Curie temperature plotted for $GdCo_2$ is that determined by Skrabek and Wallace.[3] Significantly, two proportionality constants are required to fit the data. Thus, for a given $(g - 1)^2J(J + 1)$ the Curie temperatures are decreased in those compounds having Co moments

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(14) R. M. Moon, W. C. Koehler, and J. Farrell, *J. Appl. Phys.*, **36**, 978 (1965).

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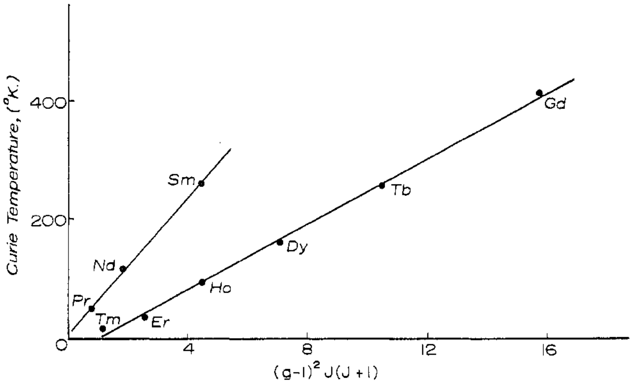

Figure 1.—Curie temperatures *vs.* $(g - 1)^2J(J + 1)$ for $LnCo_2$ compounds. The value for $GdCo_2$ is taken from Wallace and Skrabek (ref. 4).

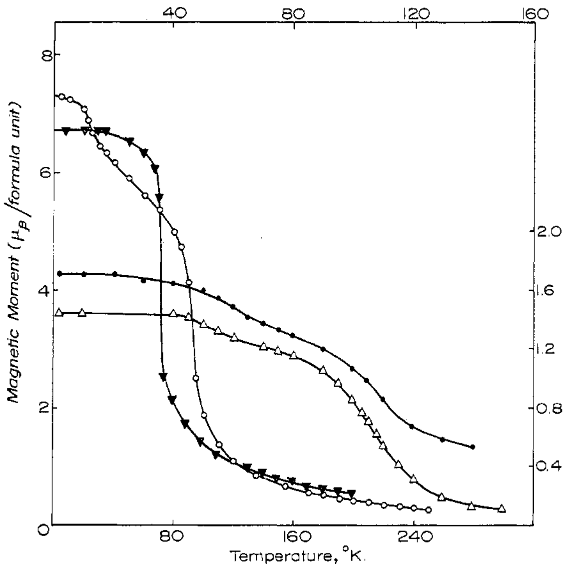

Figure 2.—Magnetic moments (measured at 19.3 koersteds) *vs.* temperature for $NdCo_2$ (△), $SmCo_2$ (●), $HoCo_2$ (○), and $ErCo_2$ (▼). The upper scale applies to $NdCo_2$ and $ErCo_2$; the lower scale is for the Sm and Ho compounds. The right-hand scale is for $SmCo_2$, and the left-hand one is for the other three compounds.

antiparallel to the lanthanide components, as compared to those in which the coupling is parallel.

From the above discussion and the data presented in Tables I, III, and IV, it is evident that the lanthanide moments are greater in the $LnCo_2$ series than in the $LnNi_2$ series. These higher moments can be attributed in part to the fact that the presence of local Co moments strengthens the molecular fields and results in a more complete mixture of crystal field states. In addition, the interatomic distances are larger for a given $LnCo_2$ compound than for the corresponding nickel compound. Since these compounds are conductors and a shielded Coulomb potential is involved, the increase in distance, even though slight, could greatly diminish the strength of the interaction with the crystal field. It seems very clear that exchange is the dominant interaction in the cobalt series, and in this respect the situation is different from that in the $LnNi_2$ compounds. Hence, the different degree of quenching is not unexpected.

The cobalt compounds exhibit a number of unusual features: (1) results for $NdCo_2$, $SmCo_2$, and $HoCo_2$ (Figure 2) indicate that these materials lose their ferromagnetism in two stages; (2) C–W behavior is not observed for $PrCo_2$ and $HoCo_2$; (3) C–W behavior is exhibited in other cases ($NdCo_2$, $DyCo_2$, and $ErCo_2$), but the slope lends itself to no simple interpretation; (4) for $TmCo_2$ a compensation point is observed at about 120°K.; (5) the Co moment is variable, ranging from about zero when its Ln partner is nonmagnetic to about 1 μ_B per atom when united with a strongly magnetic lanthanide.

There seems little likelihood that the unusual characteristics of the $LnCo_2$ compounds can be fully elucidated at this time. Since cobalt carries a moment (at least in some members of the series), one encounters in attempts to interpret the magnetic behavior of these compounds the same problems that are encountered in dealing with the elemental 3d transition metals. The Co–Co distance in the compounds is nearly that for elemental cobalt. In consequence, the behavior of the 3d electrons in these Laves phases is probably closely akin to that in pure cobalt in the sense that they are neither localized nor itinerant but rather are in some ill-defined intermediate state. Under these circumstances it would probably be fortuitous if the cobalt 3d electrons responded so as to produce C–W behavior and contributed to the Curie constant in a normal way. The situation is further complicated by the possibility of electron transfer from the lanthanide to the cobalt component and by the powerful magnetic and exchange fields generated by the strongly magnetic lanthanide ions. In YCo_2 and $CeCo_2$, where the lanthanide is nonmagnetic, the cobalt moment is zero or nearly so. Evidently, electron transfer has occurred from the strongly electropositive lanthanide to the cobalt ions until their 3d shells are full, or nearly so. However, when the lanthanide is strongly magnetic, there is a sizable cobalt moment. Presumably, this occurs since it is energetically more favorable for a magnetic lanthanide to have a magnetic partner with which it can couple. To a first approximation, the cobalt moment can be related to the molecular field in the compound, a point to which Bleaney first drew attention.[26] From the foregoing remarks it should be clear that analysis of the magnetic behavior of the $LnCo_2$ compounds involves not only the usual problems of the 3d metals but, in addition, brings in special features having to do with interactions between the Ln and Co sublattices.

There are three compounds which follow the C–W law. The value of the Curie constants is as if there were no Co moment in $ErCo_2$; in the others the observed Curie constants indicate effective moments of 3.6 and 4.0μ_B/Co for $NdCo_2$ and $DyCo_2$, respectively. In view of the circumstances set forth in the preceding paragraphs, it does not seem profitable at this time to attempt an interpretation of the effective moments of Co in these three compounds; nor does it seem appropriate to attempt an analysis of the failure of the other compounds to exhibit C–W behavior.

The magnetization–temperature behavior is anoma-

(26) B. Bleaney, ref. 2, p. 499.

lous not only for the Nd, Sm, Ho, and Tm compounds, as indicated above, but also for $ErCo_2$, 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 $ErCo_2$, 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 byRoss and Crangle[11] in their study of these compounds and by Walline and Wallace[27] in their investigation of NdNi and HoNi.

In YCo_2 and $CeCo_2$ 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 YCo_2 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 YCo_2 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 $CeCo_2$ 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.

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Platinum–Tin Metal Clusters

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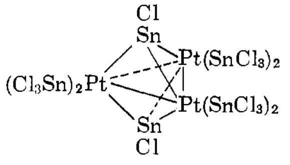
A complex anion, $[Pt_3Sn_8Cl_{20}]^{-4}$, has been obtained by reaction of stannous chloride with $PtCl_2$ or with $[Cl_2Pt(SnCl_3)_2]^{-2}$ in acetone. Salts of this new anion react with 1,5-cyclooctadiene to give a neutral compound, $(C_8H_{12})_3Pt_3Sn_2Cl_6$. Both the anion and the neutral complex are believed to be derivatives of a Pt_3Sn_2 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 $[Cl_2Pt(SnCl_3)_2]^{-2}$ and $[Pt(SnCl_3)_5]^{-3}$ anions have been isolated[2-4] from solutions of these chlorides in dilute hydrochloric acid and in methanol.

Examination of the products formed from $SnCl_2$ and $PtCl_2$ in acetone solution has now shown the existence of a third anionic complex, $[Pt_3Sn_8Cl_{20}]^{-4}$. Salts of this species, in contrast to those of $[Pt(SnCl_3)_5]^{-3}$, are stable to air and can be recrystallized from a number of solvents. Treatment of $[Pt_3Sn_8Cl_{20}]^{-4}$ solutions with 1,5-cyclooctadiene gives a neutral compound, $(C_8H_{12})_3Pt_3Sn_2Cl_6$.



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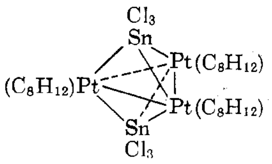

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These complexes are formulated as derivatives of a Pt_3Sn_2 metal cluster, a trigonal bipyramid with platinum atoms in the equatorial plane and tin atoms at the apices. In the anionic complex I, two $SnCl_3^-$ groups are coordinated to each platinum, 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 $[Pt_3Sn_8Cl_{20}]^{-4}$ salts, a very strong band appears at 330 cm.$^{-1}$, a frequency which is characteristic of σ-bonded $SnCl_3^-$ groups in the mononuclear complexes.[5,6] This absorption is absent in the cyclooctadiene complex which has, instead, bands

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