^{61}Ni was assumed to be negative.

The line widths observed in the single-crystal spectra are very small even at room temperature. The contributions to the line width which must be considered are (a) unresolved ligand hfs interactions, (b) electron spin–lattice relaxation processes, and (c) small lattice distortions giving rise to a distribution of the paramagnetic molecules over a small range of orientations. The room-temperature line width estimated from the relaxation data for $(n\text{-Bu}_4\text{N})[\text{Ni/Au(mnt)}_2]$ agrees very well with the experimental one. A similar good agreement was observed for $(n\text{-Bu}_4\text{N})[\text{Pt/Au(mnt)}_2]$.[12] In the latter case the Raman relaxation rate is faster, which results in a larger line width than observed for the Ni(III) complex. Therefore, spin–lattice interactions are mainly responsible for the room-temperature line width. An additional line width contribution can be caused by hyperfine interactions with protons of the $(n\text{-Bu}_4\text{N})^+$ counterions or with ligand protons for the xdt systems. In the mnt complexes these interactions will not give a noticeable contribution because of the large metal–proton distances. For the xdt or dmi-t complexes a small contribution of approximately 10^{-4} cm^{-1} can be observed from the counterion protons if the $(n\text{-Bu}_4\text{N})^+$ groups are placed in the fifth and/or sixth coordination positions of the coordination sphere. Unfortunately, no structural data are available for these complexes. Line width contributions arising from lattice distortions can be considered as being very small for the mnt and dmi-t chelates since no line width variation was observed when the crystals were rotated. The xdt chelates show a small line width variation; however, since the structure of $(n\text{-Bu}_4\text{N})[\text{Cu(xdt)}_2]$ is unknown, this variation cannot be attributed unambiguously to lattice distortions without consideration of unresolved proton hyperfine interactions.

The long spin–lattice relaxation times (T_1(300 K) $\approx 10^{-6}$–10^{-7} s) are the result of (a) a low value of the Debye temperature and (b) the high metal–ligand covalency in the molecules of these molecular crystals. Analogous[30–34] results have been obtained from experimental and theoretical relaxation studies on copper(II) bis(dialkyldichalcogenocarbamates) which are similar to the dithiolene chelates concerning their bonding properties.

Preliminary crystal structure work on $(n\text{-Bu}_4\text{N})[\text{Au(mnt)}_2]$ has shown that this complex is isomorphous with the analogous Cu(III) complex. Therefore, it is not surprising that weak metal–metal pair lines appear in the EPR spectra even for higher doped crystals. From the relaxation experiments the pair relaxation rate was found to be greater than the relaxation rate of the "single Ni^{3+} ions". This is not unexpected since due to the greater number of energy levels present in pairs there exist more possibilities for the energy transfer from the pairs to the lattice than for "single ions". As a result, pairs relax faster than "single ions".[32]

Acknowledgment. We wish to thank Professor Dr. S. A. Altshuler and Dr. B. V. Solovev (Physics Department, State University, Kazan, USSR) for their help in measuring the relaxation data. We are indebted to Dr. S. Wartewig (Physics Department, Karl Marx University, Leipzig) and to Dr. J. Sieler (Chemistry Department, Karl Marx University, Leipzig) for helpful discussions concerning the MO calculations and for communication of preliminary crystal structure data of $(n\text{-Bu}_4\text{N})[\text{Au(mnt)}_2]$.

Registry No. $(n\text{-Bu}_4\text{N})[\text{Ni(dmi-t)}_2]$, 68401-88-7; $(n\text{-Bu}_4\text{N})[\text{Pd(dmi-t)}_2]$, 73712-40-0; $(n\text{-Bu}_4\text{N})[\text{Pt(dmi-t)}_2]$, 73712-42-2; $(n\text{-Bu}_4\text{N})[\text{Au(dmi-t)}_2]$, 73712-44-4; $(n\text{-Bu}_4\text{N})[\text{Ni(mnt)}_2]$, 18958-62-8; $(n\text{-Bu}_4\text{N})[\text{Ni(xdt)}_2]$, 15338-39-3; $(n\text{-Bu}_4\text{N})[\text{Pd(xdt)}_2]$, 73712-46-6; $(n\text{-Bu}_4\text{N})[\text{Au(mnt)}_2]$, 14710-21-5; $(n\text{-Bu}_4\text{N})[\text{Cu(xdt)}_2]$, 15442-44-1; $(n\text{-Bu}_4\text{N})_2[\text{Ni(dmi-t)}_2]$, 72022-67-4; $(n\text{-Bu}_4\text{N})_2[\text{Pd(dmi-t)}_2]$, 72688-90-5; $(n\text{-Bu}_4\text{N})_2[\text{Pt(dmi-t)}_2]$, 72688-91-6; $C_3S_5(COC_6H_5)_2$, 68494-08-6; $HAuCl_4$, 16903-35-8.

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^{31}P[^{1}H] Nuclear Magnetic Resonance Investigation of Gold Cluster Compounds

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^{31}P[^{1}H] NMR spectra of gold–phosphine clusters—$\text{Au}_8(\text{PAr}_3)_8^{2+}$, $\text{Au}_9(\text{PAr}_3)_8^{3+}$, $\text{Au}_{11}(\text{PAr}_3)_7\text{X}_3$, and $\text{Au}_{11}(\text{PAr}_3)_8\text{Y}_2^+$ (X = SCN, I; Y = SCN, Cl)—show only one singlet, which is explained by a dominant trans influence of the central gold atom upon the chemical shifts of the phosphines coordinated to peripheral gold atoms. $\text{Au}_{11}[\text{P}(p\text{-ClC}_6\text{H}_4)_3]_7(\text{SCN})_3$–$\text{PPh}_3$ mixtures in C_6D_6 show a complex pattern which is interpreted as the result of the presence of $\text{Au}_{11}\text{L}'_{7-n}\text{L}_n(\text{SCN})_3$ clusters ($\text{L}' = \text{P}(p\text{-ClC}_6\text{H}_4)_3$, $\text{L} = \text{PPh}_3$, $0 \le n \le 7$) in which different phosphines are coordinated to one cluster. Spectra of $\text{Au}_{11}\text{L}'_{7-n}\text{L}_n(\text{SCN})_3$ (n = 0–2) mixtures can be interpreted by assuming that L couples with all L′ phosphines with the same coupling constant. From this it is concluded that the coupling is mainly transmitted through the central gold atom.

Introduction

In the course of our work on gold clusters, chemical analyses and conventional spectroscopic methods (e.g., IR) were found to be of limited use to identify and to verify purity of gold clusters. ^{31}P NMR spectroscopy, however, proved to be very useful and became the main analytical tool in our work. This technique was also used to investigate reactions of gold–phosphine clusters[1–3] and to obtain information about chemical bonding and dynamical properties of these compounds.

Experimental Section

The following gold clusters were prepared according to known procedures: $\text{Au}_8(\text{PAr}_3)_8^{2+}$ by the reaction of $\text{Au}_9(\text{PAr}_3)_8^{3+}$ with an excess of PAr$_3$;[2] $\text{Au}_9(\text{PAr}_3)_8^{3+}$ by the reduction of $\text{Au}(\text{PAr}_3)\text{NO}_3$ with NaBH$_4$;[5] $\text{Au}_{11}(\text{PAr}_3)_7\text{X}_3$ by the reduction of $\text{Au}(\text{PAr}_3)\text{X}$ with NaBH$_4$;[4] $\text{Au}_{11}(\text{PAr}_3)_8\text{Y}_2^+$ by the reaction of $\text{Au}_9(\text{PAr}_3)_8^{3+}$ with Y$^-$.[1] ^{31}P NMR

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(1) F. A. Vollenbroek, J. J. Bour, J. M. Trooster, and J. W. A. van der Velden, *J. Chem. Soc., Chem. Commun.*, 907 (1978).

(2) F. A. Vollenbroek, W. P. Bosman, J. J. Bour, J. H. Noordik, and P. T. Beurskens, *J. Chem. Soc., Chem. Commun.*, 387 (1979).

(3) F. A. Vollenbroek, Thesis, Nijmegen, 1979, and to be submitted for publication.

(4) F. Cariati and L. Naldini, *Inorg. Chim. Acta*, **5**, 172 (1971).

(5) F. Cariati and L. Naldini, *J. Chem. Soc., Dalton Trans.*, 2286 (1972).

(6) F. A. Vollenbroek, P. C. P. Bouten, J. M. Trooster, J. P. van den Berg, and J. J. Bour, *Inorg. Chem.*, **17**, 1345 (1978).

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Table I. $^{31}P[^1H]$ NMR Data of Gold-Phosphine Clusters, Mononuclear Gold Complexes, and Free Phosphines

compd	NMR, ppm[a]	
	C_6D_6	CD_2Cl_2
$Au_{11}[PPh_3]_7(SCN)_3$	+49.5	+49.9
$Au_{11}[P(p\text{-}ClC_6H_4)_3]_7(SCN)_3$	+48.0	
$Au_{11}[P(p\text{-}MeC_6H_4)_3]_7(SCN)_3$	+48.0	
$Au_{11}[P(p\text{-}ClC_6H_4)_3]_7I_3$	+48.2	
$Au_{11}[P(p\text{-}FC_6H_4)_3]_7I_3$	+47.5	
$[Au_{11}(PPh_3)_8(SCN)_2]PF_6$		+50.7
$[Au_{11}(PPh_3)_8Cl_2]PF_6$		+50.2
$[Au_9(PPh_3)_8](PF_6)_3$		+54.8
$[Au_9(P(p\text{-}MeC_6H_4)_3)_8](PF_6)_3$		+53.5
$[Au_8(PPh_3)_8](PF_6)_2$		+53.0
$Au(PPh_3)NO_3$		+25.1
$Au(PPh_3)Cl$		+31.0
$Au(PPh_3)SCN$		+34.8
$[Au(PPh_3)_2]PF_6$		+42.6
PPh_3	−8.3	
$P(p\text{-}ClC_6H_4)_3$	−11.4	
$P(p\text{-}MeC_6H_4)_3$	−10.8	
$P(p\text{-}FC_6H_4)_3$	−11.8	

[a] Relative to $OP(OMe)_3$ (TMP) reference (upfield = minus); all singlets apart from the septet of PF_6.

spectra were recorded on a Varian XL-100-FT spectrometer using the deuterated solvent as an internal lock. $OP(OMe)_3$(TMP) was used as an external standard; however, when this reference compound was added to the gold cluster, no reaction or deviation from the calculated chemical shift was observed.

Results

(a) $^{31}P[^1H]$ NMR Investigation of Gold-Phosphine Clusters in Which Only One Type of Phosphine Is Present. The proton-decoupled ^{31}P NMR spectra ($^{31}P[^1H]$ NMR) of all investigated gold-phosphine clusters show only one singlet. In Table I a list of the measured shifts is given. All singlets are very sharp (line width 3 Hz) except for the singlet of $[Au_8L_8]^{2+}$ (L = PPh_3), which is rather broad (line width 25 Hz). Low-temperature measurements down to −90 °C of $Au_{11}L'_7(SCN)_3$ (L′ = $P(p\text{-}ClC_6H_4)_3$) (toluene-*d*) and $[Au_9L_8](PF_6)_3$ (CD_2Cl_2) show no line broadening. The gold cluster $[Au_8L_8](PF_6)_2$, which shows a broad line at room temperature, does not show further broadening or sharpening on cooling (CD_2Cl_2). The simplicity of the $^{31}P[^1H]$ NMR spectra is remarkable in view of the fact that the crystal structure determinations revealed nonequivalent gold-phosphine sites in all clusters investigated[2,7,8] (see Figure 1).

The observed singlets may be caused either by a dynamic equilibration of the phosphine ligands which in the crystalline state were geometrically distinct or by an (accidental) equal chemical shift. Upon addition of L′ to a C_6D_6 solution of $Au_{11}L'_7(SCN)_3$, the cluster gives a sharp singlet at +48.0 ppm and the free phosphine one at −11.4 ppm. This reveals that no fast exchange of the phosphine ligands with free phosphine occurs on the ^{31}P NMR time scale, so such intermolecular processes cannot be the origin of an equilibration. Furthermore from the low-temperature measurements it seems less likely that intramolecular processes, in which ligands migrate over the cluster surface or in which Au(peripheral)-ligand entities change their positions, are interconverting the gold-phosphine sites. Apparently the shift differences between the various gold-phosphine sites are too small to be detected with the apparatus used (Varian XL-100-FT; ^{31}P 40.5 MHz). At the moment there is no reasonable explanation for the broadened singlet of $[Au_8L_8]^{2+}$.

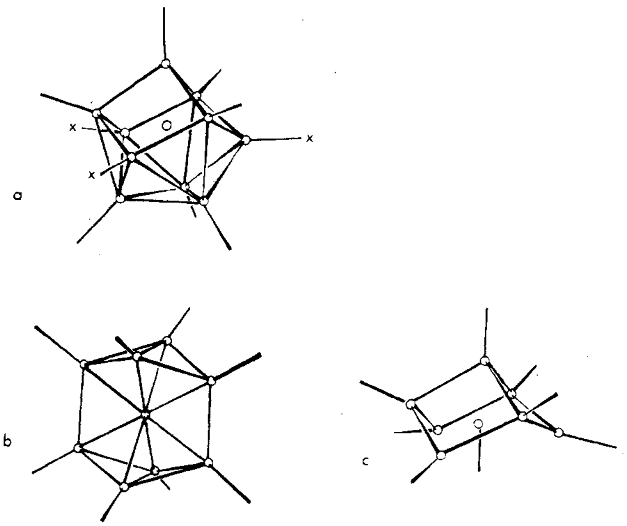

Figure 1. (a) $Au_{11}L_7X_3$; for $Au_{11}L_8Y_2^+$ one of the X ligands is substituted by a L. (b) $Au_9L_8^{3+}$. (c) $Au_8L_8^{2+}$.

The small chemical shift differences of the phosphines that are coordinated to peripheral gold atoms suggest that these shifts are mainly determined by the atom in trans position to the phosphorus atoms, which is the central gold atom for all phosphorus atoms, and that cis influences through peripheral gold-gold interactions are small. This is in agreement with the interpretation of the Mössbauer data which lead to the conclusion that the peripheral gold atoms are linearly hybridized and that peripheral interactions tangential to the polyhedral surface are small.[6,9]

The important role of the central gold for the chemical shifts of the phosphines coordinated to the peripheral gold atoms is demonstrated by the fact that substitution of a PPh_3 by a SCN^- ligand, from $[Au_{11}L_8(SCN)_2]^+$ to $Au_{11}L_7(SCN)_3$, changes the chemical shifts of all remaining phosphines equally: the difference in nature of the SCN^- ligand as compared with the substituted PPh_3 ligand is transmitted to all other Au-P sites exclusively via the central gold atom.

The chemical shifts of the cluster-coordinated phosphines are in a rather small range: $Au_{11}L_7(SCN)_3$ +49.9; $[Au_{11}L_8Cl_2]^+$ +50.2; $[Au_{11}L_8(SCN)_2]^+$ +50.7; $[Au_8L_8]^{2+}$ +53.0; $[Au_9L_8]^{3+}$ +54.8 ppm (CD_2Cl_2). For mononuclear complexes larger shift differences are observed: $AuLNO_3$ +25.1; AuLCl +31.0; AuLSCN +34.8; AuL_2^+ +42.6 ppm (CD_2Cl_2). It is noteworthy that substitution of Cl by SCN and of SCN by L results in a downfield shift both in the mononuclear compounds and in the clusters.

The chemical shift difference between free PPh_3 and coordinated PPh_3 is larger for gold-phosphine clusters (+58 to +63 ppm) than for mononuclear gold-phosphine compounds (+33 to +51 ppm) (see Table I). A possible reason for this might be that the phosphines have a larger σ donation to the gold atoms in the clusters than to the gold atoms in mononuclear gold(I) complexes. This would be in accord with the low contribution of the cluster to the isomer shift and quadrupole splitting of the peripheral gold atoms in the Mössbauer spectra of the clusters;[9] i.e. the small donation of cluster electrons to the peripheral gold atoms makes a somewhat larger donation of the coordinated phosphines possible.

(b) $^{31}P[^1H]$ NMR Investigation on $Au_{11}L'_{7-n}L_n(SCN)_3$ (L′ = $P(p\text{-}ClC_6H_4)_3$, L = PPh_3, $0 \leq n \leq 7$). As mentioned above no fast-exchange reaction can be observed when L′ is added to a C_6D_6 solution of $Au_{11}L'_7(SCN)_3$. Similarly when L is added to a C_6D_6 solution of $Au_{11}L_7(SCN)_3$, no fast-exchange

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(7) P. L. Bellon, F. Cariati, M. Manassero, L. Naldini, and M. Sansoni, *Chem. Commun.*, 1423 (1971).

(8) P. L. Bellon, M. Manassero, and M. Sansoni, *J. Chem. Soc., Dalton Trans.*, 1481 (1972).

(9) F. A. Vollenbroek, J. W. A. van der Velden, J. J. Bour, and J. M. Trooster, to be submitted for publication.

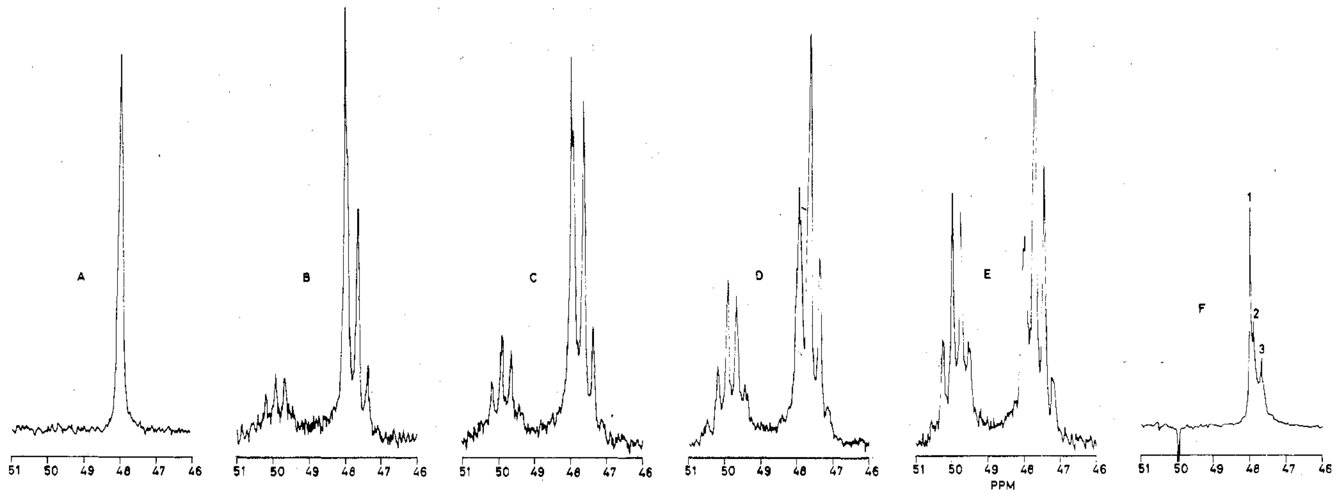

Figure 2. $^{31}P[^1H]$ NMR spectra of $Au_{11}L'_7(SCN)_3$–L mixtures (C_6D_6) (recorded 24 h after mixing): (A) $Au_{11}L'_7(SCN)_3$; (B) $Au_{11}L'_7(SCN)_3$ + 1L; (C) $Au_{11}L'_7(SCN)_3$ + 2L; (D) $Au_{11}L'_7(SCN)_3$ + 3L; (E) $Au_{11}L'_7(SCN)_3$ + 4L. Homonuclear decoupled $^{31}P[^1H]$ NMR spectrum of (F) $Au_{11}L'_7(SCN)_3$ + 1L (corresponding with the spectrum of Figure 2B).

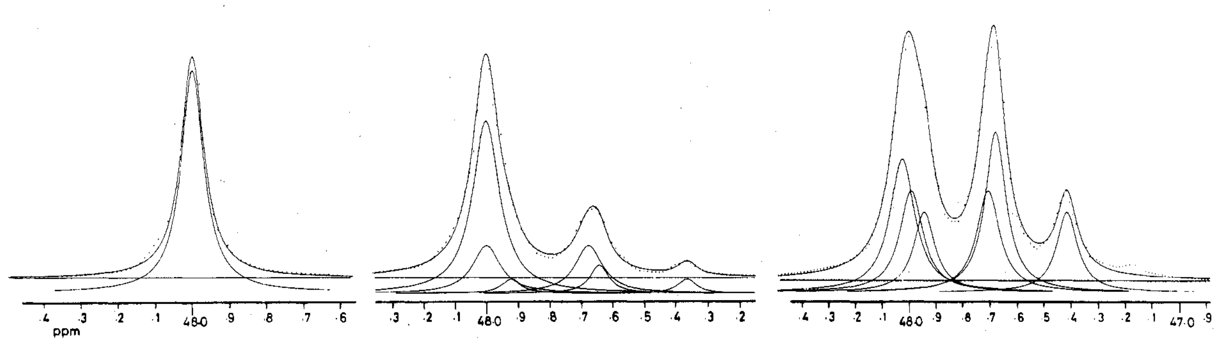

Figure 3. Least-squares fits of the right-hand side of the spectra shown in Figure 2A–C (2A corresponds with 3A etc.)

reaction is observed. $Au_{11}L_7(SCN)_3$ gives a singlet at +49.5 ppm relative to TMP and L gives a singlet at −8.3 ppm (position of free L). However, when L is added to a C_6D_6 solution of $Au_{11}L'_7(SCN)_3$ or when L′ is added to a C_6D_6 solution of $Au_{11}L_7(SCN)_3$, apart from the singlets of free L and L′, two multiplets appear in the spectra centered near the original singlet positions at +49.5 and +48.0 ppm.

In Figure 2A–E spectra are shown which were recorded 24 h after addition of 0, 1, 2, 3, and 4 equiv of L, respectively, to 1 equiv of $Au_{11}L'_7(SCN)_3(C_6D_6)$ (the singlets of free L and L′ are not shown). When 4 L is added to 1 $Au_{11}L'_7(SCN)_3$, the spectra recorded at increasing time intervals after mixing are similar to those shown in Figure 2. Obviously the substitution of L′ on $Au_{11}L'_7(SCN)_3$ by L proceeds slowly relative to the NMR time scale but reaches an equilibrium within 24 h. The infrared spectra of the mixtures (recorded in C_6D_6) all show one SCN vibration at 2105 cm^{-1} indicating that no thiocyanate ligands are substituted.

Saturation of the multiplet at the left-hand side of the spectrum in Figure 2B in a homonuclear decoupling experiment—meanwhile maintaining the heteronuclear decoupling—simplifies the right-hand side of the spectrum to three singlets (see Figure 2F). From this it can be concluded that the right-hand side of the spectrum in Figure 2B contains multiplets due to coupling of phosphorus atoms of L and L′ coordinated to the same cluster. Singlet 1 (see Figure 2F) has the same position as was found for $Au_{11}L'_7(SCN)_3$ and is also present in the nondecoupled spectrum. The other singlets (2 and 3) are probably due to the mono- and disubstituted compounds $Au_{11}L'_6L(SCN)_3$ and $Au_{11}L'_5L_2(SCN)_3$, respectively.

The observed chemical shift differences between the singlets of the L′ phosphines of $Au_{11}L'_7(SCN)_3$, $Au_{11}L'_6L(SCN)_3$, and $Au_{11}L'_5L_2(SCN)_3$ in the homonuclear decoupled spectrum (singlets 1, 2, and 3 in Figure 2F) are much smaller (6 and 9 Hz) than the shift difference which is observed upon substitution of a SCN^- ligand by phosphine: from $Au_{11}L_7(SCN)_3$ to $[Au_{11}L_8(SCN)_2]^+$ the shift difference is +32 Hz (+0.8 ppm) (see Table I). This in accord with the smaller difference in ligand character between L and L′ as compared to L and SCN^-.

A least-squares analysis was made of the right-hand side of the spectra of Figure 2A–C. It was assumed that L couples with all L′ phosphines with the same coupling constant, $Au_{11}L'_6L(SCN)_3$ giving a doublet and $Au_{11}L'_5L_2(SCN)_3$ giving a triplet. The results of these fits are given in Figure 3A–C, where the dots represent the right-hand side of the spectra of Figure 2A–C, respectively. The drawn line is the least-squares fitted spectrum. The Lorentzian components of the calculated spectra are shown somewhat shifted downward with respect to the base line. The spectrum of Figure 3A (pure $Au_{11}L'_7(SCN)_3$) was fitted with one line for which a line width of 3 Hz was found. The line position found (+48.0 ppm) was kept fixed in the fits of the other spectra (Figure 3B,C). In these fits the line intensities of the two lines of the doublet were kept at 1:1 and those of the three lines of the triplet at 1:2:1. The positions of the corresponding lines and their line widths were found to be the same for both least-squares fits. Only the singlet:doublet:triplet intensity ratios are different.

As discussed above the right-hand side of the spectrum of Figure 2B simplifies to three singlets upon mononuclear decoupling. Singlet 1 in Figure 2F corresponds with the singlet used in the least-squares fits, singlet 2 corresponds with the doublet, and singlet 3 corresponds with the triplet. The P–P coupling constants found from the least-squares fits are 14 Hz in the doublet and 11 Hz in the triplet. In the literature no P–P couplings for gold compounds are reported. We have observed a ${}^3J$ coupling of 8 Hz in the compound $[(Ph_3P)_2C(AuPPh_3)_2](NO_3)_2$ which was prepared by the reaction of $Ph_3P{=}C{=}PPh_3$ with $AuPPh_3NO_3$ (ratio 1:2).[10]

The fact that the spectra of mixtures of $Au_{11}L'_7(SCN)_3$, $Au_{11}L'_6L(SCN)_3$, and $Au_{11}L'_5L_2(SCN)_3$ can be fitted very well with a singlet, doublet and triplet suggests that the assumption, which was made, i.e., L couples with all L′ with the same coupling constant, is reasonable. This would mean that the coupling of L with L′ is transmitted equally to all L′ ligands even though they are in different positions with respect to L. As mentioned in section a, the temperature-dependent experiments which have been performed on the Au_8, Au_9, and Au_{11} clusters, did not indicate any dynamic behavior to be a probable mechanism for the equivalence of the magnetic environment of the phosphorus atoms. This indicates that the coupling is mainly transmitted through the central gold atom. This is in accord with the conclusions from the single-line ${}^{31}P[{}^1H]$ NMR spectra and the Mössbauer results:[6,9] the linearly hybridized peripheral gold atoms have no direct two-center bonds through which the P–P couplings can be transmitted. In this view the P–P couplings over the Au_{11} cluster are to be described as ${}^4J$ couplings.

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Registry No. $Au_{11}[PPh_3]_7(SCN)_3$, 12583-03-8; $Au_{11}[P(p\text{-}ClC_6H_4)_3]_7(SCN)_3$, 65982-55-0; $Au_{11}[P(p\text{-}MeC_6H_4)_3]_7(SCN)_3$, 12583-09-4; $Au_{11}[P(p\text{-}ClC_6H_4)_3]_7I_3$, 12582-97-7; $Au_{11}[P(p\text{-}FC_6H_4)_3]_7I_3$, 37871-66-2; $[Au_{11}(PPh_3)_8(SCN)_2]PF_6$, 69787-01-5; $[Au_{11}(PPh_3)_8Cl_2]PF_6$, 69787-02-6; $[Au_9(PPh_3)_8](PF_6)_3$, 38999-04-1; $[Au_9(P(p\text{-}MeC_6H_4)_3)_8](PF_6)_3$, 34754-43-3; $[Au_8(PPh_3)_8](PF_6)_2$, 72271-21-7; $Au(PPh_3)NO_3$, 14897-32-6; $Au(PPh_3)Cl$, 14243-64-2; $Au(PPh_3)SCN$, 14243-61-9; $[Au(PPh_3)_2]PF_6$, 73872-15-8; PPh_3, 603-35-0; $P(p\text{-}ClC_6H_4)_3$, 1159-54-2; $P(p\text{-}MeC_6H_4)_3$, 1038-95-5; $P(p\text{-}FC_6H_4)_3$, 18437-78-0.

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[10] F. A. Vollenbroek and J. M. Trooster, to be submitted for publication.

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Negative Oxidation States of the Chalcogens in Molten Salts. 1. Raman Spectroscopic Studies on Aluminum Chlorosulfides Formed in Chloride and Chloroaluminate Melts and Some Related Solid and Dissolved Compounds

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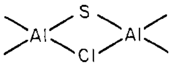
Raman spectroscopic measurements on series of LiCl–CsCl and $CsCl–AlCl_3$ melts have shown that dissolved tetrachloroaluminate and sulfide ions at temperatures around 400 °C react in a ratio close to 1:1, forming clear solutions sometimes with gel precipitates. Preliminary potentiometric measurements on basic $CsCl–AlCl_3$ melts have shown the average chloride–sulfide exchange number to be 2.0 ± 0.1. A glassy compound, $(CsAlSCl_2)_\infty$, was prepared, indicating in conjunction with other evidence the probable existence of a homologous series of chainlike ions $[Al_nS_{n-1}Cl_{2n+2}]^{n-}$ with $n \geq 3$ and polymeric $[AlSCl_2]_n^{n-}$ (for large n). These ions are characterized by a strong polarized Raman band near 325 cm⁻¹, assignable to the $AlCl_2–S–AlCl_2$ units. In neutral and acidic chloroaluminate melts the ions dissociate, forming dissolved species such as $[Al_nS_{n-1}Cl_{2n+2-m}]^{(n-m)-}$ and solid AlSCl. The solutions give a polarized Raman signal near 292 cm⁻¹ which can be assigned to the doubly bridged



units within the ions. The Raman spectra of AlSCl and some other related solids are reported. The general aspects of the findings are discussed in connection with limited Raman studies on selenium- and bromide-substituted systems, which probably are quite analogous.

Introduction

The nature of sulfur and sulfides dissolved in chloroaluminate melts is rather complex and at present only partially understood. Sulfur reacts with alkali metals and aluminum, forming sulfides and polysulfides often of varying *non*stoichiometric composition.

A few experiments have previously been conducted on sulfur in molten salt systems. The solubilities and redox reactions of some metal sulfides have been studied in LiCl–CsCl eutectic mixtures at temperatures around 400 °C.[2-8] More recently, the electrochemistry of sulfur and sulfide in sodium tetrachloroaluminate melts was examined[9-11] at 175 °C and found to be highly dependent on the melt composition, according to the proposed reaction (1) in conjunction with the acid–base

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[1] Visiting professor from State University of New York at Old Westbury.

[2] Delarue, G. *Bull. Soc. Chim. Fr.* **1960**, 906, 1654.

[3] Bodewig, F. G.; Plambeck, J. A. *J. Electrochem. Soc.* **1969**, *116*, 607; **1970**, *117*, 618, 904.

[4] Gruen, D. M.; McBeth, R. L.; Zielen, A. J. *J. Am. Chem. Soc.* **1971**, *93*, 6691.

[5] Giggenbach, W. *Inorg. Chem.* **1971**, *10*, 1308.

[6] Liu, C. H.; Zielen, A. J.; Gruen, D. M. *J. Electrochem. Soc.* **1973**, *120*, 67.

[7] Bernard, J. P.; de Haan, A.; Van der Poorten, H. *C. R. Hebd. Seances, Acad. Sci., Ser. C* **1973**, *276*, 587.

[8] Cleaver, B.; Davies, A. J.; Schiffrin, D. J. *Electrochim. Acta* **1973**, *18*, 747.

[9] Marassi, R.; Mamantov, G.; Chambers, J. Q. *J. Electrochem. Soc.* **1976**, *123*, 1128. Marassi, R.; Mamantov, G.; Matsunaga, M.; Springer, S. E.; Wiaux, J. P. *Ibid.* **1979**, *126*, 231.

[10] Paulsen, K. A.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1976**, *98*, 6866.

[11] Robinson, J.; Gilbert, B.; Osteryoung, R. A. *Inorg. Chem.* **1977**, *16*, 3040.

0020-1669/80/1319-2688$01.00/0