Inorg. Chem. **1981**, *20*, 2623–2626

Contribution from the Chemistry Department,
Furman University, Greenville, South Carolina 29613

Generation of Scandium Dichloride, Dibromide, and Dicyanide Radicals by Codeposition Reactions in Argon Matrices at 14 K: An Electron Spin Resonance Investigation

L. B. KNIGHT, JR.,* M. B. WISE, and T. A. FISHER

Received September 19, 1980

Codeposition reactions between Sc and Cl_2, Br_2, and $(CN)_2$ have been conducted in argon matrices at 14 K. Results are compared with previous codeposition studies of simple metallic radicals and with gas-phase reactions. Radical products generated have been identified and investigated via electron spin resonance (ESR). The magnetic parameters are as follows: $ScCl_2$, $g = 1.983$ (3), $A(^{45}Sc) = 200$ (6) MHz; $ScBr_2$, $g = 1.970$ (3), $A(^{45}Sc) = 197$ (9) MHz, $A(^{79}Br) = 22$ (2) MHz; $Sc(CN)_2$, $g = 1.980$ (1), $A(^{45}Sc) = 201$ (3) MHz.

Introduction

Group 2A, 2B, and 3B metals have been codeposited with halogen and $(CN)_2$ molecules in argon matrices in an effort to determine reaction products, to compare matrix codeposition results with gas-phase reactions, to further characterize the matrix codeposition reaction process for simple systems, and to generate MX- and MX_2-type radicals for electronic structure studies via ESR spectroscopy. Codeposition reactions previously reported are compared with these new findings.

Application of the rare-gas matrix ESR method for the study of small inorganic radicals has been reviewed elsewhere.[1] The codeposition procedure that was applied in early matrix isolation experiments has proven to be a valuable technique for generating radicals of interest that are not readily produced by the simple vaporization of a stable precursor.[2] For example, no high-temperature vaporization scheme is known that produces group 2A monohydrides. However, the codeposition of metal atoms and thermally generated hydrogen atoms under suitable experimental conditions does form isolated MH radicals.[3-5] Whether reaction takes place in the gas phase (after mixing with argon) just prior to condensation or whether it occurs in rapidly forming matrix cages is not known. However, the matrix does act to quench a certain fraction of reactants before complete reaction to MH_2 occurs. For the matrix codeposition systems studied, no information is available concerning the relative amounts of the various atomic and molecular species trapped. Also, metal aggregates probably form at the high concentration levels required for most codeposition reactions.

Apparently no previous investigations of $ScCl_2$, $ScBr_2$, and $Sc(CN)_2$ have been reported except for recent gas-phase chemiluminescence experiments for the dihalides.[6] Matrix codeposition generation of the CdCN, HgCN, and $Y(CN)_2$ radicals has been reported.[7,8] The ScX_2 radicals are highly ionic and appear to be bent with the unpaired electron localized primarily in a metal 3d orbital. Overall, their electronic structure is similar to ScF_2 with a slight increase in covalent character observed for the heavier halogens.[9] The "simple" d^1-type transition-metal molecules are useful model cases for study since complicated effects such as spin–spin interactions are absent. Only a few d^1 cases have been reported; these include ScF_2,[9] TiF_3,[10] MnO_3,[11] and TiF_2^+.[12] Most of the metallic radicals studied via matrix ESR have been the hydrides, oxides, and fluorides. The experimental results of this study are useful in establishing the effects of systematic variation of the ligand for a given metal atom.

Table I. Magnetic Parameters (MHz) for MX_2 Radicals in Argon at 14 K[a]

	g	A		g	A
ScF_2[b]	1.995 (1)	220 (3)	$ScBr_2$	1.970 (3)	197 (9)
^{19}F		28 (2)	^{79}Br		22 (2)
YF_2[c]	1.990 (1)	748 (3)	$Sc(CN)_2$	1.980 (1)	201 (3)
^{19}F		87 (2)	$Y(CN)_2$[c]	1.973 (2)	672 (3)
$ScCl_2$	1.983 (3)	200 (6)			
^{35}Cl		4[d]			

[a] The signs of the A values cannot be determined from these experiments. [b] Reference 9. [c] Values are A_{iso} and g_{iso}; see ref 8. [d] Splitting not resolved; the figure shown represents the maximum value.

Experimental Section

The Dewar-furnace arrangement, the ESR equipment, and the closed-cycle helium refrigerator have been previously described.[13] Matrix gases were Matheson research grade, and Sc metal (99.99%) was obtained from Alfa Inorganics. Typical matrix gas deposition rates employed were 14–18 mmol h^{-1}. The Sc metal effusion cell was constructed from $^1/_4$-in. tantalum tube and was located 15 cm from the sapphire rod deposition target. The argon matrix gas doped with the reactant molecules (Cl_2, 5%; Br_2, 3%; $(CN)_2$, 3%) was directed toward the deposition surface from a single nozzle about 3 cm away. Significantly weaker ESR signals resulted for concentrations less than 2 mol % while much broader signals were observed for concentrations greater than 5%. The codeposition of Sc from the resistively heated cell at 1650 K with the matrix–halogen mixture was typically conducted for a 20-min period. Numerous experiments were conducted in the same manner except the resulting matrices were photolyzed with a 100-W Hg resonance lamp at 2537 Å for approximately 5 min.

Several codeposition experiments between I_2 and Sc were conducted. Because of the low vapor pressure of iodine, gas mixtures of I_2 and argon were not employed. Alternatively, the argon inlet tube had a side arm equipped with a high-vacuum valve. Iodine crystals were placed in the side arm. Judging from the changes produced on a thermocouple gauge mounted in the argon line, we deduced that various amounts of $I_2(g)$ were admitted into the argon gas flow. It

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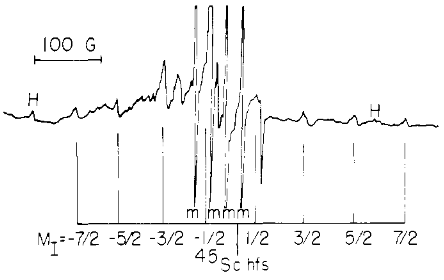

Figure 1. ESR spectrum of $ScCl_2$ in argon at 14 K. The magnetic field corresponding to g_e occurs at the center of the methyl quartet denoted by "m". Modulation (100 kHz) was 2 G, and incident microwave power was approximately 1.0 mW for all spectra presented.

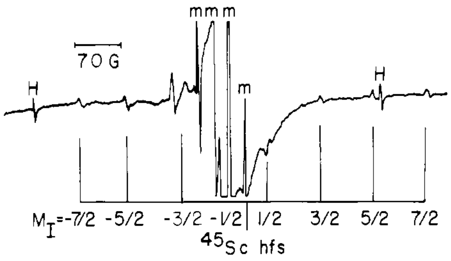

Figure 2. ESR spectrum of $Sc(CN)_2$ in argon at 14 K. The magnetic field corresponding to g_e occurs at the center of the methyl quartet denoted by "m".

was difficult to accurately determine the resulting I_2 percentages, but values over a wide range (1–20%) were tried on a series of eight separate codeposition experiments.

Results

The resulting ESR spectra for the codeposition reaction of Sc + Cl_2 and Sc + $(CN)_2$ are shown in Figures 1 and 2, respectively. Table I gives the observed magnetic parameters for the ESR spectra assigned to these radicals. Eight lines are expected for the hyperfine splitting of ^{45}Sc (100% abundance; $I = {}^7/_2$; $\mu = 4.749$ nm). For the ScF_2 radical, the Sc hfs was 220 (3) MHz in argon.[9] Values similar to this are expected for the other highly ionic ScX_2 radicals. The ESR signals are quite weak and broad but do form a recognizable octet pattern with a definite second-order increase in the splitting going from low to high field. The experimental line positions fit the usual second-order solutions to the axial spin Hamiltonian within the experimental uncertainty of 2 G.[14] Strong methyl radical and other impurity signals were also observed that did not correlate with the MX_2 signals on various experiments or for various microwave power settings.

The chlorine hfs is not resolvable for $ScCl_2$, but its effect apparently contributes to the unusual width of the signals. If the same percent fluorine spin density in ScF_2 occurs for Cl in $ScCl_2$, the ^{35}Cl hfs would be approximately 10% of that observed for ^{19}F, which was only 10 G. Therefore a Cl hfs of approximately 1 G is not expected to produce a resolvable pattern.

Fortunately, for ^{79}Br (50%; $I = {}^3/_2$; $\mu = 2.099$ nm) and ^{81}Br (50%; $I = {}^3/_2$; $\mu = 2.2626$ nm) the same percent halogen spin density observed for ScF_2 is expected to produce larger hfs, which might be resolvable. The overall ESR spectrum of $ScBr_2$ also consisted of an octet pattern with an ^{45}Sc hfs similar to the other ScX_2 radicals. However, each member of the octet pattern for $ScBr_2$ did exhibit additional bromine hfs. Figure 3 represents an expanded-scale spectrum of the lowest field ^{45}Sc octet line. Since the bromine hfs is small, differences due to the two isotopes with slightly different magnetic moments are not clearly resolved. Therefore a seven-line pattern is expected as if two magnetically equivalent bromine atoms were present. A similar splitting pattern is observed for all eight of the ^{45}Sc hyperfine transitions. As was the case for ScF_2, **g** tensor and **A** tensor anisotropy was not observed or resolved for $ScBr_2$.

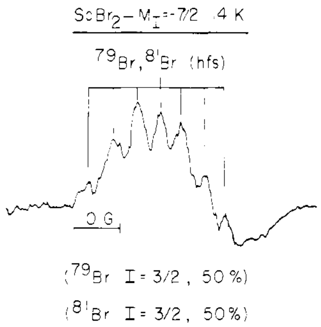

Figure 3. Expanded-scale ESR spectrum of the lowest field ^{45}Sc transition of $ScBr_2$ exhibiting Br hfs. The center of the seven-line pattern occurs at 3202 G. Spectrometer frequency is 9526 MHz.

The ^{45}Sc hyperfine lines for $Sc(CN)_2$ are nearly isotropic and considerably narrower. This is expected since the ^{14}N hfs for the CN^- ligand should be less than 1 G.[7] Codeposition alone did not produce the ESR signals attributed to $Sc(CN)_2$. Photolysis of the codeposited matrix sample was required to generate $Sc(CN)_2$ radicals, which also produced intense CN radical ESR signals.[15] By contrast, photolysis of the $ScCl_2$ and $ScBr_2$ matrices caused the ESR signals of these radicals to disappear. Prior to photolysis of the Sc + $(CN)_2$ matrix, a very complex pattern was observed in the $g = 2$ area, which is tentatively assigned to scandium clusters, probably Sc_3. This same complex pattern was observed with and without the presence of $(CN)_2$ but diminished significantly during photolysis as the $Sc(CN)_2$ signals grew. Additional ESR experiments are planned to more fully investigate metal cluster formation for scandium and other metals.

Even though numerous Sc + I_2 experiments were conducted, definite assignment of the ScI_2 radical could not be made. Signals attributed to quenched I atoms were observed for the more concentrated Sc argon matrices. A study of quenched I atoms in a xenon matrix has recently been reported.[16] A detailed treatment of our I atom argon results will be presented later.

On almost all high-temperature matrix depositions methyl radicals and H atoms are detected. Their intensity is usually observed to increase dramatically upon UV photolysis. Although the sources of such impurities are not known for certain, they probably arise from the cracking of diffusion or mechanical pump fluids. Organic impurities in the reactive gases employed might also be present, which could produce CH_3 and H radicals upon pyrolysis and/or photolysis.

Discussion

Codeposition Formation of Metallic Radicals. Table II lists simple metallic radical molecules generated by codeposition reactions. Cases that do not lead to radical formation under similar experimental conditions are marked with an "X". For example, the codeposition reaction Y + F_2 does not produce YF_2. However, the YF_2 radical has been produced by the high-temperature vaporization-reduction of YF_3(s). None of the metals shown produce radicals when codeposited with H_2. Reactions that do not produce the indicated radical without photolysis are marked "*hν*". Important matrix codeposition reactions known to produce more complex metallic radicals

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Table II. Radical Formation Results for Metallic Codeposition Reactions in Rare Gas Matrices

Be	Mg	Al
$Be + H \rightarrow BeH^a$ $Be + F_2 \rightarrow BeF^a$ $Be + Cl_2 \rightarrow BeCl^a$ $Be + Br_2 \rightarrow BeBr^a$ $Be + H_2O_2 \rightarrow BeOH^m$ $Be + CH_3I \nrightarrow BeI$ or $BeCH_3{}^a$	$Mg + H \rightarrow MgH^a$ $Mg + F_2 \rightarrow MgF^a$ $Mg + Br_2 \rightarrow MgBr^a$ $Mg + H_2O_2 \rightarrow MgOH^c$	$Al + H \nrightarrow AlH_2{}^a$ $Al + F_2 \nrightarrow AlF_2{}^a$ $Al + O_2 \nrightarrow AlO^a$

Sc	Y	La
$Sc + F_2 \nrightarrow ScF_2{}^a$ $Sc + Cl_2 \rightarrow ScCl_2$ $Sc + Br_2 \rightarrow ScBr_2$ $Sc + (CN)_2 \xrightarrow{h\nu} Sc(CN)_2$	$Y + F_2 \nrightarrow YF_2{}^a$ $Y + Cl_2 \nrightarrow YCl_2{}^a$ $Y + Br_2 \nrightarrow YBr_2{}^a$ $Y + (CN)_2 \rightarrow Y(CN)_2{}^a$	$La + F_2 \nrightarrow LaF_2{}^a$

Zn, Cd, Hg	Cr	Fe
$(Zn, Cd, Hg) + H \rightarrow MH^d$	$Cr + H \rightarrow CrH + CrH_2{}^k$	$Fe + F_2 \xrightarrow{h\nu} FeF_3{}^e$
$(Zn, Cd) + F_2 \rightarrow MF^a$ $Hg + F_2 \xrightarrow{h\nu} HgF^a$ $(Cd, Hg) + CN \rightarrow MCN^l$ $Zn + Br_2 \rightarrow ZnBr^a$	$Cr + F_2 \xrightarrow{h\nu} CrF + CrF_3{}^e$	

Mn	Si	Pd,[j] Yb[b]	Ag
$Mn + H \rightarrow Mn + MnH_2{}^f$ $Mn + F_2 \xrightarrow{h\nu} MnF + MnF_2{}^e$ $Mn + N_2O \xrightarrow{h\nu} MnO^g$ $Mn + O_2 \rightarrow MnO_2{}^g$ $Mn + O_3 \rightarrow MnO + MnO_2 + MnO_3{}^g$	$Si + N_2 \rightarrow SiN_2{}^h$ $Si + CO \rightarrow SiCO^h$	$M + H \rightarrow MH$	$Ag + (Zn, Cd, Hg, Mg, Ca, ...) \rightarrow AgM^i$

[a] Results from this laboratory; in press or to be published. [b] Reference 4. [c] Reference 27. [d] Reference 28. [e] Reference 29. [f] Reference 30. [g] Reference 31. [h] Reference 32. [i] Reference 33. [j] Reference 34. [k] Reference 5. [l] Reference 7. [m] Reference 26.

not listed in Table II include metal–organic adduct,[17] alkali-water,[18] and ion-pair radical reactions.[19] Considerably more work, both experimental and theoretical, is required before generalized predictions can be made, but hopefully the summary in Table II will serve as a useful guide for generating other radical systems. The production of simple model compounds for the heavier metals of the second and third transition rows and the lanthanides and actinides should be feasible.

Very few of the reactions listed in Table II have been studied under well-defined conditions in the gas phase. Comparisons of such gas-phase studies with matrix codeposition results might yield more detailed information about the dynamics of the matrix reaction process. It is interesting to compare a series of recently reported gas-phase chemiluminescence reactions conducted under single-collision conditions with the matrix results of this study. The only combinations of group 3B metals with halogens that produced gas-phase chemiluminescence evidence for the formation of the MX_2 radical are $ScCl_2$, $ScBr_2$, and ScI_2.[6] Reactions with $(CN)_2$ have not been conducted. The combinations tried for the matrix codeposition experiment are listed in Table II. Therefore, for those systems studied by both methods, similar results have been obtained.

Chemical Bonding Trends. g Tensors. Formally, one would assign the unpaired electron for the highly ionic MX_2-type radical to the *n*d orbital of the M^{2+} ion. The geometry of ScF_2 and YF_2, determined from vibrational analysis, is C_{2v} with a bond angle of ~135°.[20,21] The geometry of $ScCl_2$, $ScBr_2$, and $Sc(CN)_2$ has not been previously determined. If these heavier halogen radicals were linear, the $3d_{xy}$ and $3d_{x^2-y^2}$ orbitals would be degenerate and a $^2\Delta$ electronic ground state would most likely occur (see discussion for the ScF_2 case).[9] Since the observed g values are close to the free-spin value and hence not consistent with such a ground-state assignment, the radicals are probably bent. Bending would probably lower the $3d_{xy}$ orbital relative to the $3d_{x^2-y^2}$, thereby quenching the orbital angular momentum, and produce an approximate g value of 2.0. A definite bond angle cannot be determined from these studies.

Using the axially symmetric approximation and assuming that the observed lines are the perpendicular transitions, we can use the following expression to estimate $\Delta g_\perp$:

$$\Delta g_\perp = g_\perp - g_e = -2\lambda C_1{}^2 C_2{}^2/\Delta E$$

where λ is the spin–orbit constant of a Sc 3d electron and ΔE is the energy separation between the ground and excited electronic states. The factor "2" applies since coupling would occur between the ground d_{xy} (or $d_{x^2-y^2}$) orbital and an excited d_{xz} or d_{yz} orbital. Additional terms similar to the above would be required to consider coupling to other excited states. The $C_1{}^2$ factor represents the amount of d_{xy} character in the ground state and $C_2{}^2$ the excited-state d_{xz} or d_{yz} character. The $\Delta g_\perp$ values for ScF_2, $ScCl_2$, and $ScBr_2$ of −0.007, −0.019, and −0.032, respectively, form an interesting progression. The fact that $\Delta g_\perp$ is negative indicates dominant spin–orbit coupling to vacant excited states. An interesting question in exploring this series is whether changing the halogen atom indirectly affects the spin–orbit coupling on the metal ion (C_2, for example) or whether halogen orbitals are directly involved. A more complete **g** tensor expression would involve halogen orbital contributions and spin–orbit parameters.[15] There is a correlation between $\Delta g_\perp$ and the halogen spin–orbit parameter, which increases from approximately 270 to 590 to 2500 cm^{-1} for F, Cl, and Br, respectively.[23] These atomic spin–orbit numbers for neutral ground-state atoms are only rough indications of the relative increase expected since it is not known which orbitals are actually involved. Also the net charge on the halogen atom will tend to reduce the spin–orbit constants. Indirect effects such as electronic changes in the metal orbital ground-state composition or changes in energy level separations are not likely to be large enough to produce the $\Delta g_\perp$ changes. The constancy of the ^{45}Sc hfs (the *A* parameter) suggests that large ground-state orbital shifts do not occur. Large changes in energy level separations are not usually observed for such ionic compounds as the halogen atom is changed. For example, the low-lying excited states in CaF, CaCl, and CaBr occur at approximately the same energies above the ground state.[23] One interesting conclusion of this highly qualitative analysis is that excited-state covalent effects will have to be considered to account for the observed $\Delta g_\perp$ trend. The individual $\Delta g_\perp$ values are small and difficult to treat, given matrix effects and lack of excited-state information. However, the trend of Δg values for these radicals with the

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same metal atom seems to establish a definite relationship to the halogen ligands. The results for $Sc(CN)_2$ are somewhat inconsistent with the others since CN^- has a small spin–orbit constant, yet the $\Delta g_\perp$ value lies between $ScCl_2$ and $ScBr_2$. It appears that the CN^- ligand substantially lowers the excited-state metal ion energy levels, thereby enhancing the metal spin–orbit coupling. One could also argue that it more radically alters the excited-state metal orbital composition. In either case, it seems that indirect effects on the spin–orbit coupling are more important for CN^- than for the halogen ligands. A similar large decrease in $\Delta g_\perp$ of 0.015 is observed for CdCN[7] relative to CdF.[13] An even larger decrease of 0.092 occurs for the HgCN[7] and HgF[24] pair of radicals. Hopefully, detailed electronic measurements will corroborate these **g** tensor predictions that the excited states of metallic cyanides occur at significantly lower energies than do these of the corresponding halides.

Examples of Δg changes for the same ligands but for different metals can be seen for the ScF_2–YF_2 and $Sc(CN)_2$–$Y(CN)_2$ cases given in Table I. Variation in Δg ascribable to the metal change is approximately −0.006 for both cases. This is smaller than might be predicted on the basis of the metal spin–orbit parameter, which increases by nearly a factor of 3.5 for yttrium over scandium.[22] Also, the excited states for Y^{2+} are lower lying than for Sc^{2+}. However, it has been established that the amount of metal "s" character is nearly 10 times greater for the yttrium radicals than for scandium, thereby implying considerably less "d" character, which would be eligible for spin–orbit coupling in the yttrium radicals.

A Tensors. The A values for $ScCl_2$, $ScBr_2$, and $Sc(CN)_2$ are compared to those of ScF_2, YF_2, and $Y(CN)_2$ from previous studies in Table I. Since only one component of an apparently anisotropic spectrum is observed or resolved for all three radicals, it is not possible to unambiguously determine the individual isotropic and anisotropic contributions to the metal hfs. Using the axially symmetric approximation and assuming that the component observed is the "perpendicular" transition, we can use the following analysis to estimate orbital spin densities:

$$A_\perp = A_{\mathrm{iso}} - A_{\mathrm{dip}} \qquad A_\parallel = A_{\mathrm{iso}} + 2A_{\mathrm{dip}}$$

$$A_{\mathrm{iso}} = {}^8\!/_3\pi g_e g_n \beta_e \beta_n |\psi(0)|^2$$

$$A_{\mathrm{dip}} = g_e g_n \beta_e \beta_n \left\langle \frac{3\cos^2\theta - 1}{2r^3} \right\rangle$$

Various values of A_{dip} for a Sc $3d_{xy}$ or $3d_{x^2-y^2}$ electron range from approximately −60 to −70 MHz.[25] A reviewer has suggested that $A_\parallel$ might be approximately zero, causing the "parallel" features to occur in the unresolved center portion of the spectrum. Although this possibility cannot be eliminated, it is not supported by the spectra observed for ScF_2 where the $g = 2$ region was relatively free of unassigned lines. It is certainly not uncommon for the weaker "parallel" components to go undetected. Using an atomic A_{iso} of 2820 MHz for the "4s" level of Sc, assuming $A_\parallel$ was approximately zero, and using the observed $A_\perp$ value of 200 MHz, one would obtain 4s and 3d spin densities of 5% and 97%, respectively. An alternate approach that does not speculate on the magnitude of $A_\parallel$ is to observe that even the maximum atomic value for A_{dip} is small. Hence, $A_\perp \approx A_{\mathrm{iso}}$ produces a 4s spin density estimate of 7%. By difference one could estimate a 3d spin density of 93%. Hence both approximations produce comparable results. An A_{iso} value for Sc^{2+} [$(4s)^1$; ^2S] of ~5000 MHz does not significantly alter the above qualitative conclusions.[25]

The ligand hfs in ScF_2, YF_2, and $ScBr_2$ can be resolved while that for $ScCl_2$, $Sc(CN)_2$, and $Y(CN)_2$ cannot. The small ligand hfs demonstrates that the ligands have essentially closed shells and electron transfer to them is nearly complete. Numerous previous studies have shown the validity of this conclusion for F ligands; however, these are the first results that demonstrate that the heavier halogen atoms behave similarly. Resolution of the $ScBr_2$ ligand hfs into parallel and perpendicular components was not possible.

Recently, the ScH_2, YH_2, and YD_2 radicals have been generated and trapped in argon matrices.[35] For ScH_2 and YH_2, the metal **A** tensor was unambiguously resolved into parallel and perpendicular components. The unpaired electron occupies almost exclusively the metal d_{xy} orbital with practically no metal "s" character.

Acknowledgment. Support from NSF Grant CHE-7910134 and the Research Corp. Cottrell College Science Program is gratefully acknowledged. The use of an ESR spectrometer under DOE Contract CE-AC 09-76SR00827 is greatly appreciated.

Registry No. $ScCl_2$, 23693-73-4; $ScBr_2$, 15607-70-2; $Sc(CN)_2$, 77661-64-4.

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