

corresponding angles in the pyridine N-oxide complex. The two oxygen atoms are within 2.32 Å of each other, somewhat shorter than the O–O distance of 2.37 Å in the pyridine N-oxide complex. Since chloride ions are much larger than oxygen atoms, chlorine–chlorine and chlorine–oxygen repulsions should cause a significant decrease in the O–Cu–O angle in a pseudo-planar structure. The Cu–O distances of 2.01 and 1.98 Å in $\text{Cu}_3\text{Cl}_6(\text{C}_6\text{H}_7\text{NO})_2 \cdot 2\text{H}_2\text{O}$ are similar to the values of 2.04 and 1.98 Å found in the pyridine N-oxide complex and 1.97 and 1.93 Å found in the yellow form of dichlorobis-(2,6-lutidine N-oxide)copper(II).¹⁶

The N–O bond distance is 1.36 Å and the bond lies 1.9° out of the plane of the 2-picoline ring. The long N–O distance is consistent with loss of double-bond character owing to complex formation. In the pyridine N-oxide complex, the N–O bond lies 8.4° from the plane defined by the copper and oxygen atoms, whereas in the 2-picoline N-oxide complex the N–O bond makes an angle of 13.5° with the copper–oxygen plane. The angle of the 2-picoline ring relative to the copper–oxygen plane is 88.8° while the pyridine ring made an angle of 70.0° relative to the copper–oxygen plane. The 2-picoline ring is planar, and a least-squares fit with the atoms weighted relative to their atomic number showed the largest deviation from the plane to be 0.010 Å. This is smaller than the estimated standard deviations of the ring carbon atoms. The average C–N bond length is 1.37 Å and the average C–C distance is 1.38 Å. The bond distances around the ring are too inac-

(16) R. S. Sager and W. H. Watson, submitted for publication.

curate for individual distances to be discussed. If one considers the carbon–carbon bonds to be chemically equivalent, it appears that the estimated standard deviations in some cases are optimistic by a factor of about 2.

The observed magnetic susceptibility data can be interpreted in terms of the structure. The structure can be thought of as consisting of alternating $\text{Cu}_2\text{Cl}_4(\text{C}_6\text{H}_7\text{NO})_2$ units and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ units joined by long (2.955 and 2.654 Å) Cu–Cl bonds. The copper ions in the $\text{Cu}_2\text{Cl}_4(\text{C}_6\text{H}_7\text{NO})_2$ units interact antiferromagnetically through the bridging oxygens. The copper ions of the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ units do not interact through the chloride bridges with the five-coordinated copper ions and therefore show normal magnetic behavior. Thus the entire complex has an experimental magnetic moment slightly greater than that expected for an isolated copper ion.^{1,5} The moment varies only slightly as the temperature is lowered from room temperature to 77°K. Since $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ undergoes an antiferromagnetic transition at 4.3°K, it should be interesting to investigate the magnetic susceptibility of $\text{Cu}_3\text{Cl}_6(\text{C}_6\text{H}_7\text{NO})_2 \cdot 2\text{H}_2\text{O}$ below liquid nitrogen temperatures.

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Synthesis and Magnetic Resonance Studies of Some Paramagnetic Transition Metal Aminotroponimines

By D. R. EATON, W. R. McCLELLAN, AND J. F. WEIHER

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The synthesis and proton magnetic resonance spectra of a number of aminotroponimine chelates of the first-row transition metals—V, Cr, Mn, Fe, and Co—are reported. The majority of these complexes are paramagnetic and show large Fermi contact shifts in their nmr spectra. The interpretation of these shifts in terms of metal-to-ligand and ligand-to-metal charge transfer is considered.

Introduction

The observation and interpretation of the very large chemical shifts associated with protons on the ligands of paramagnetic transition metal complexes has proved to be a fruitful source of information regarding the electronic nature of metal–ligand bonding. In cases where the large chemical shifts can be ascribed to Fermi contact interaction between unpaired electron spin and nuclear spin of the proton, the results can be interpreted in terms of electron spin density distributions. This is

a concept made familiar by electron spin resonance studies of aromatic radicals. The important point for the present purpose is that the spin density distribution corresponding to a given molecular orbital can be easily calculated, at least to a qualitatively reliable approximation, and comparison of such calculations with experimental results hopefully will allow identification of the spin-containing ligand molecular orbital. Using this information, deductions can then be made regarding metal–ligand orbital interactions and bonding.

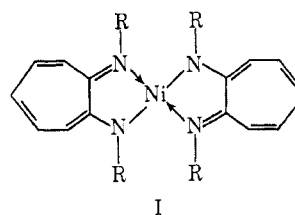
In previous work this approach has been applied to nickel(II) aminotroponiminates¹ and to a variety of transition metal acetylacetonates.² The aminotroponimate ligand is a complex molecule, and difficulties in the unambiguous assignment of the resonance and in the interpretation of the shifts might be anticipated. However, for the Ni(II) complexes two circumstances simplify the situation. First, the lines are very sharp, allowing the resolution of spin-spin coupling which is a great aid in the assignment problem; and, second, a single shift-producing mechanism appears to be dominant, namely, delocalization of spin by ligand-to-metal charge transfer in the π system. For the acetylacetonates, on the other hand, the simplicity of the ligand eliminates most of the assignment problems, but a multiplicity of spin delocalization mechanisms were found to be necessary to account for the observed shifts. From this previous work the conclusion emerged that the most important factor in determining these metal-ligand interactions was the relative energies of the metal d and ligand π orbitals. Specifically, at the beginning of the transition metal series [Ti(III), V(III)] the d orbitals are relatively high in energy and well placed to interact with a low-lying antibonding π orbital of the acetylacetonate ligand. Toward the end of the series [Ni(II)] the metal d orbitals are lower in energy and are correctly situated to interact with a rather high-energy-filled π orbital of the aminotroponimate ligand. When different ligands are present in the same chelate, it was also demonstrated that the splitting of the d orbital degeneracies due to reduced symmetry of the complex could also have an important bearing on the mode of spin delocalization.^{3,4}

The present work was aimed at the extension and confirmation of some of the observations noted above. Specifically, two areas seemed worthy of further development. In the series of first-row transition metal acetylacetonates, although metal-to-ligand charge transfer was sufficient to account for the results at the beginning of the series [Ti(III), V(III)], it was found necessary to postulate an additional contribution from ligand-to-metal charge-transfer processes at the end of the series. The aminotroponimate ligand is more prone to participate in ligand-to-metal charge transfer, and it appears that this is the exclusive process for the Ni(II) complexes. One might ask, though, whether on passing to earlier transition metals evidence would be found for metal-to-ligand charge transfer which would make the behavior of aminotroponimine as a ligand entirely complementary to that of acetylacetonate. To investigate this possibility, first, aminotroponimate chelates of V(III) (d^2), Cr(III) (d^3), Mn(III) (d^4), Fe(III) (d^5), Fe(II) (d^6), and Co(II) (d^7) have been examined and the results were compared with those previously obtained for Ni(II) (d^8). Second, in nickel chelates with two different aminotro-

ponimine ligands it has been shown that the different ligands compete to donate electrons to the metal.³ Since the aminotroponimate is considered to prefer to donate π electrons and the acetylacetonate ligand is considered to prefer to accept π electrons, it is of interest to study their mutual interactions in mixed chelates. Unfortunately, the Ni(II) chelates with one acetylacetonate ligand and one aminotroponimate ligand are square planar and diamagnetic. However, results have been obtained for analogous mixed chelates of V(III) and of Mn(III). We have previously studied mixed chelates of V(III) with acetylacetonate and hexafluoroacetylacetonate⁴ and interpreted the results in terms of splitting the d-orbital degeneracies.

Preparation of Transition Metal(II) and -(III) Chelates

Methods analogous to those used⁵ for preparation of nickel chelates of N,N'-disubstituted aminotroponimines (I) (abbreviated R₂ATI), give, in the ab-



sence of oxygen, the paramagnetic Co(II) chelates of N,N'-diethylaminotroponimine ((C₂H₅)₂ATI) and of diaryl ATI's and they also give the diamagnetic Co(III) chelate of (CH₃)₂ATI. The Co(II) chelates are sensitive to oxygen and react slowly with certain chlorinated solvents such as CHCl₃ or CH₂Cl₂. As previously reported,⁶ the Fe(II) chelates are not obtained by these procedures, but reaction of anhydrous FeCl₂ with N-lithioaminotroponimines in the absence of oxygen gives the paramagnetic Fe(II) chelates of (C₂H₅)₂ATI and of diaryl ATI's and the Fe(III) chelate of (CH₃)₂ATI. Similarly, ((C₂H₅)₂ATI)₂Mn^{II} and (diaryl ATI)₂Mn^{II} are obtained, but ((CH₃)₂ATI)₃Mn^{III} compounds are obtained by reaction of anhydrous MnCl₂ with lithio derivatives of the ATI's. The Mn(II) and Fe(II) chelates of ATI react with oxygen (both in solution and in the solid state⁷), water, alcohols, and chlorinated hydrocarbons. It appears that in all cases M(III) compounds are formed.

Reaction of anhydrous CrCl₂ with lithio derivatives of (CH₃)₂ATI, (C₂H₅)₂ATI, and diaryl ATI's gives, in all cases, the Cr(III) chelate.

Paramagnetic ((CH₃)₂ATI)₃V and ((C₂H₅)₂ATI)₃V are prepared by reaction of VCl₃ with the corresponding ATI in THF in the presence of pyridine. The former chelate is formed readily at room temperature in good yield while the latter is obtained only after refluxing the reaction mixture for several hours and then in low yield.

Products from reaction of ATIs with Fe(CO)₅,⁸ Mn₂(CO)₁₀, and Cr(CO)₆ parallel those obtained from reac-

(1) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962).

(2) D. R. Eaton, *J. Am. Chem. Soc.*, **87**, 3097 (1965).

(3) D. R. Eaton and W. D. Phillips, *J. Chem. Phys.*, **43**, 392 (1965).

(4) D. R. Eaton, to be submitted for publication.

(5) W. R. Brasen, H. E. Holmquist, and R. E. Benson, *J. Am. Chem. Soc.*, **83**, 3125 (1961).

(6) W. R. McClellan and R. E. Benson, *ibid.*, **88**, 5165 (1966).

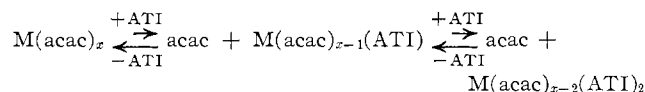
(7) Reaction products of ((C₂H₅)₂ATI)₂Fe and oxygen will be discussed in a separate paper.

tion of lithio derivatives of ATIs with the anhydrous metal dihalides as detailed above.

The fact that $((\text{CH}_3)_2\text{ATI})_3\text{M}^{\text{III}}$ compounds are easily prepared while, in most cases, the corresponding M(III) chelates of $(\text{C}_2\text{H}_5)_2\text{ATI}$ and diaryl ATI are not obtained is attributed to the difficulty in spatial accommodation of three ATI ligands by a metal atom if the groups attached to the nitrogens are larger than methyl. The easy formation of $((\text{C}_2\text{H}_5)_2\text{ATI})_3\text{Cr}^{\text{III}}$ appears to be an unexplained exception. The mechanism of formation of the trivalent metal chelates in reaction of the lithio derivative of $(\text{CH}_3)_2\text{ATI}$ with MnCl_2 or CrCl_2 probably involves reaction of $((\text{CH}_3)_2\text{ATI})_2\text{M}^{\text{II}}$ with $(\text{CH}_3)_2\text{ATI}$ as postulated⁶ for the formation of $((\text{CH}_3)_2\text{ATI})_3\text{Fe}^{\text{III}}$. The very reactive $((\text{CH}_3)_2\text{ATI})_2\text{Mn}^{\text{II}}$ and $((\text{CH}_3)_2\text{ATI})_2\text{Cr}^{\text{II}}$ compounds could possibly be prepared, as was the case⁶ with the corresponding Fe(II) derivative, by trapping them as a complex with a material such as pyridine.

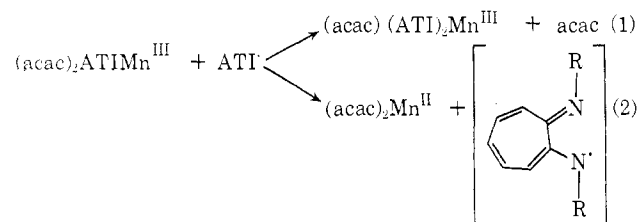
Study of Mixed Acetylacetonate acac-ATI Chelates

Mixed ATI-acac chelates of Ni(II), Pd(II), Fe(III), Mn(III), V(III), and Mo(III) have been prepared by ligand exchange starting with the metal acetylacetonate. In general, the equilibrium highly favors formation of the metal acac, and no mixed chelate is detected by nmr on addition of ATI's to metal acetylacetonates as in



where $x = 2$ or 3 . However, by heating a mixture of ATI with $\text{M}(\text{acac})_x$ under reduced pressure to remove acac as it is formed, mixed chelates have been prepared where $\text{M} = \text{Ni}(\text{II}), \text{Pd}(\text{II}), \text{Fe}(\text{III}), \text{Mn}(\text{III}), \text{V}(\text{III}),$ or $\text{Mo}(\text{III})$. The second acac moiety is harder to remove than the first and higher temperatures and longer heating periods are required; the third has been removed only with $(\text{CH}_3)_2\text{ATI}$ as the ATI.

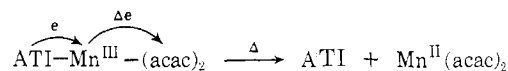
Anomalous results were obtained with Mn(III) in two respects. First, $(\text{acac})_2\text{ATIMn}^{\text{III}}$ forms as the preferred species on mixing $(\text{acac})_3\text{Mn}^{\text{III}}$ with ATI in solution at room temperature. Second, on heating $(\text{acac})_2\text{ATIMn}^{\text{III}}$ with ATI under reduced pressure, two competitive reactions occur



(1) is the predominant reaction where ATI = diaryl ATI's and (2) is the predominant reaction where ATI = $(\text{C}_2\text{H}_5)_2\text{ATI}$.

The Mn atom in an $(\text{ATI})_2\text{Mn}^{\text{II}}$ chelate readily loses an electron to give an Mn^{III} species, while $(\text{acac})_2(\text{ATI})\text{Mn}^{\text{III}}$ chelates are converted on heating to

$(\text{acac})_2\text{Mn}^{\text{II}}$ with the Mn atom gaining an electron. This apparent anomaly might not be unexpected on the basis that the ATI moiety donates π electrons to the metal which should have the effect of increasing the reducing potential of the Mn atom in $(\text{ATI})_2\text{Mn}^{\text{II}}$ while the acac moiety prefers to accept π electrons from the metal atom which might conceivably set the stage for actual transfer of an electron from the ATI to Mn in $(\text{acac})_2(\text{ATI})\text{Mn}^{\text{III}}$



Experimental Section

In the preparation and isolation of the Co(II), Fe(II), Mn(II), V(III), and Mo(III) chelates, all operations were carried out under nitrogen. Most of these chelates must also be protected from air in the crystalline state. Since many of the chelates are sensitive to water, sodium-dried solvents were generally used. Solvents used in preparation of Co(II) chelates were deaerated prior to use.

Nmr data were obtained using Varian Associates A-60 and HR-60 spectrometers for the diamagnetic and paramagnetic compounds, respectively, with TMS as an internal reference. Nmr and magnetic susceptibility data on the chelates are given in Table I. Analyses and preparative details are given in Table II. Procedures used in the preparations of Fe(II) chelates of ATI's were followed in reactions of anhydrous metal chlorides with lithio derivatives of ATI's. Examples of the general reaction conditions used (1) in the preparation of the Co(II) chelates and (2) in preparation of mixed chelates using metal acetylacetonates are given below. Chelates were prepared from metal carbonyls by methods previously described⁶ for preparation of ATI chelates from $\text{Fe}(\text{CO})_5$.

Preparation of $((\text{C}_2\text{H}_5)_2\text{ATI})_2\text{Co}^{\text{II}}$.—To a stirred solution of 2.8 g (0.016 mol) of $(\text{C}_2\text{H}_5)_2\text{ATI}$ in 5 ml of CHCl_3 and 12 ml of methanol was added dropwise a solution prepared by adding 5 ml of concentrated NH_4OH to 2.8 g (0.012 mol) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in 5 ml of water. The reaction mixture was heated under reflux for 20 min, cooled to 0° , and filtered. The crude product was warmed with water, dried, and recrystallized from CHCl_3 - CH_3OH (1:1) to give 2.1 g of reddish black crystals of $((\text{C}_2\text{H}_5)_2\text{ATI})_2\text{Co}^{\text{II}}$.

Preparation of $(\text{acac})_2((\text{C}_6\text{H}_5)_2\text{ATI})\text{Mn}^{\text{III}}$.—A mixture of 5.5 g (0.020 mol) of $(\text{C}_6\text{H}_5)_2\text{ATI}$ and 7.04 g (0.020 mol) of $\text{Mn}(\text{acac})_3$ in 25 ml of xylene was heated under nitrogen at 85° for 30 min. The solvent was removed under reduced pressure at 85° . The distillation residue dissolved completely in a refluxing mixture of 50 ml of cyclohexane and 10 ml of methylcyclohexane. The addition of 50 ml of pentane to the cold extract caused the separation of 7.5 g of crude product. Recrystallization from hexane gave 3.8 g of brownish black crystals of $(\text{acac})_2((\text{C}_6\text{H}_5)_2\text{ATI})\text{Mn}^{\text{III}}$.

The distillation residue from a similar reaction was held at 130° for 30 min under 0.1 mm. Extraction as described above left 1.9 g of insoluble yellow powder, mp 248° . *Anal.* Calcd for $\text{Mn}(\text{acac})_2(\text{MnC}_{10}\text{H}_8\text{O}_4)$: N, 0; C, 47.5; H, 5.6; Mn, 21.7. Found: N, 0.17; C, 48.3; H, 5.7; Mn, 20.8. There was no lowering of the melting point on mixing with an authentic sample of $\text{Mn}(\text{acac})_2$. The extract was treated as described above to give 2.1 g of $(\text{acac})_2((\text{C}_6\text{H}_5)_2\text{ATI})\text{Mn}^{\text{III}}$ product.

Preparation of $(\text{acac})_2((\text{C}_6\text{H}_5)_2\text{ATI})_2\text{Mn}^{\text{III}}$.—A mixture of 11 g (0.040 mol) of $(\text{C}_6\text{H}_5)_2\text{ATI}$ and 7.05 g (0.020 mol) of $\text{Mn}(\text{acac})_3$ was stirred and heated to 85° for a few minutes to obtain a homogeneous melt. It was then held at 85° (10 mm) under distillation conditions until no further distillate formed (4 min). The reaction mixture was heated until, at a temperature of 130° , distillate again appeared. After 10 min at 130 – 135° , 0.036 mol of acetylacetonate was found in the distillate. The reaction product was extracted with 150 ml of refluxing benzene leaving 0.6 g of

TABLE I
 NMR BANDS (AT 60 MC/SEC) FROM TMS

Compound	Mag. Susc., B.M. (P) (Solvent)	α	β	γ	N-Substituted Aliphatic		N-Substituted Aromatic and Other			acac	
					CH ₂ (CH ₃)	CH ₃	o-	m-	p-	p-CH ₃	CH ₃
(Me ₂ ATI) ₃ V	2.85 (CS ₂)	+1210	+416	+1480	+2144		[V(acac) ₃ CH ₃ at -2144 for CH ₃ and -240 for CH]				
(Et ₂ ATI) ₃ V		+1100	+653	+1715	+20	-328					
(acac)(Me ₂ ATI) ₂ V		+1170	+370	+1450	+1900					-2650	
(acac)(Et ₂ ATI) ₂ V		+1045	+612	+1806	-1680	-433					-2722 +400
(acac)(β ₂ ATI) ₂ V	2.6 (CHCl ₃)	+1140	+429	+1860			{-1470 (3) -1310}	-575	+5		-2645 +200
(acac)(p-T ₂ ATI) ₂ V	2.4 (CHCl ₃)	+1120	+459	+1880			{-1470 (3) -1370}	-570		-380	-2650 +195
(acac) ₂ (Et ₂ ATI)V	2.6 (CHCl ₃)	-1130	+2600	-1070	+15	-475					-2600 -2390
(acac) ₂ (β ₂ ATI)V		-1288	+2560	-1995				-235	-2180	-470	-2900 -2325
(Me ₂ ATI) ₃ Cr		+4140	-400	+6140	+3430						
(Et ₂ ATI) ₃ Cr		+4412		+6470	+3115						
(Me ₂ ATI) ₃ Mo		+9980		+14,600	+2680						
(acac)(Me ₂ ATI) ₂ Mo		+9720	+750	+11,400	+3560			[Mo(acac) ₃ CH ₃ at -7600, CH at -2300]			-6690 -2300
(Me ₂ ATI) ₃ Mn	3.12	+5040	-2486	+6665	+400						[Mn(acac) ₃ CH ₃ at -1505, CH at -2300]
(acac)(β ₂ ATI) ₂ Mn ⁽⁴⁾	4.9 (CHCl ₃)	{+4425 (3) +4275}	{-1084 (3) -1000}	+6650							
(acac)(p-T ₂ ATI) ₂ Mn ⁽⁴⁾		+4290 (3)	-1118	+6600							
(acac) ₂ (Et ₂ ATI)Mn ⁽⁴⁾	4.3 (C ₆ H ₆)	+6100	-296	+8400							
(acac) ₂ (β ₂ ATI)Mn ⁽⁴⁾	4.9 (CHCl ₃) 5.06 (C ₆ H ₆)	+5500	-160	+7630							
(Me ₂ ATI) ₃ Fe	2.0 (CHCl ₃)	+2471	-1560	+3372	-922						[Fe(acac) ₃ CH ₃ at -1243, CH at +1640]
(acac)(β ₂ ATI) ₂ Fe	5.8 (CHCl ₃)	+8000	-4600	+10,900							-895
(acac) ₂ (Et ₂ ATI)Fe		+11,100	-6087	+14,300	+3500?	-850?					-1350 +1600
(Me ₂ ATI) ₃ Co	Diamagnetic				-155						
(Et ₂ ATI) ₂ Mn	5.4 (C ₆ H ₆)	+742	-585	+1303	-1110	-300					
(p-T ₂ ATI) ₂ Mn		+793	-943	+3375				-2070	-1532		+372
(Et ₂ ATI) ₂ Fe ⁽¹⁾	4.8	+3104	-7173	+6550	-5770	+3840					
(Et ₂ ATI) ₂ Co	4.2 (CH ₂ Cl ₂)	+4100	-6900	+6100	-5400	+5700					
(Et ₂ p-BrATI) ₂ Co		+4337	-6909	--	-5109	+5800					
(β ₂ ATI) ₂ Co	4.3 (CH ₂ Cl ₂)	+2710	-6800	+5190				+5900	+425	+2710	
(p-T ₂ ATI) ₂ Co	4.2 (CH ₂ Cl ₂)	+3330	-6860	+5400				+5900	+430		-1170
(acac)(β ₂ ATI)Ni	Diamagnetic		-355 to -395					-426 Aromatic [Ni(acac) ₂ -116 for CH ₃]			-76 -309
(β ₂ ATI) ₂ Pd	Diamagnetic							-421 Aromatic			
(acac)(β ₂ ATI)Pd	Diamagnetic							-440 Aromatic [Pd(acac) ₂ CH ₃ at -127, CH at -329]			-93 -125
(acac)(p-T ₂ ATI)VO	1.78 (CHCl ₃)										

Me₂ = dimethyl; Et₂ = diethyl; β ₂ = diphenyl; p-T₂ = di-p-tolyl; ATI = aminotroponeimineate; acac = acetylacetonate

(1) Data for this and several other Fe(II) ATI's reported in ref. 2

(2) Magnetic susceptibility data obtained by nmr method. D. F. Evans, J. Chem. Soc. 2003 (1959)

(3) Doublet

(4) Other resonance observed but assignments uncertain.

insoluble Mn(acac)₂. The solid recovered from the extract was recrystallized from toluene to give 4.1 g of black crystals of (acac)₂((C₆H₅)₂ATI)₂Mn^{III}.

Preparation of (acac)₂((C₆H₅)₂ATI)Mn^{III}.—A solution of 3.5 g (0.020 mol) of (C₆H₅)₂ATI and 7.05 g (0.020 mol) of Mn(acac)₃ in 15 ml of xylene was distilled under reduced pressure at 85° for about 40 min. After removal of solvent the reaction product was held under high vacuum at 85° for 20 min. This product dissolved completely in 50 ml of refluxing cyclohexane. The 6.1 g of crude product obtained by adding pentane to the cold,

extract was recrystallized from ether to give 2.8 g of black crystals of (acac)₂((C₆H₅)₂ATI)Mn^{III}.

In a reaction of 0.040 mol of (C₆H₅)₂ATI and 0.020 mol of Mn(acac)₃ in the absence of solvent, analysis indicated about 0.017 mol of acetylacetonate in the distillate collected at 85° under reduced pressure. Most of the acac was collected in the first 3 min. On heating to 130–140° for 20 min under reduced pressure, another 0.006 mol of acac was obtained. The reaction product yielded 3.3 g (80% of theoretical) of yellow powder shown to be Mn(acac)₂ by mixture melting with an authentic

TABLE II
 ANALYTICAL AND PREPARATORY DATA ON ATI AND MIXED acac-ATI CHELATES OF TRANSITION METALS

	M.P. ¹ °C.	Method of Preparation			Metal, %		N, %		C, %		H, %	
		Reactants	Solvent	Reaction Conditions	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
(Me ₂ ATI) ₂ V	311	VCl ₃ , LiATI	THF, pyridine	30°C./2 hr.	10.3	10.1	17.1	17.2	65.8	66.4	6.8	6.8
(Et ₂ ATI) ₂ V	265	VCl ₃ , LiATI	THF, pyridine	reflux/3 hr.			14.5	13.1	68.1	68.3	7.0	8.2
(acac)(Me ₂ ATI) ₂ V	229	V(acac) ₃ , ATI (1/3)	diglyme	110-115°/5 hr.	11.5	11.4	12.6	13.4	61.1	60.8	6.6	6.6
(acac)(Et ₂ ATI) ₂ V	176	V(acac) ₃ , ATI (1/3)	none	105-155°/7.5 hr.	10.2	10.6	11.2	11.0	64.9	65.4	7.4	7.5
(acac)(β ₂ ATI) ₂ V	309	V(acac) ₃ , ATI (1:2.5)	diglyme	105-155°/4 hr.	7.4	7.6	8.1	8.1	74.5	74.5	5.4	5.4
(acac)(pT ₂ ATI) ₂ V	354	V(acac) ₃ , ATI (1:1.5)	diglyme	105-155°/4 hr.	6.8	6.9	7.5	7.7	75.3	75.0	6.1	6.4
(acac)(Et ₂ ATI)V	146	V(acac) ₃ , ATI (1/3)	none	105-115°/1.5 hr.	11.8	12.3	6.6	6.7	58.5	59.0	6.9	6.9
(acac) ₂ (β ₂ ATI)V	165	V(acac) ₃ , ATI (1:1.25)	diglyme	105-125°/7 hr.	9.8	9.5	5.4	5.1	67.0	67.8	5.6	6.1
(Me ₂ ATI) ₂ Cr	332	Cr(CO) ₆ , ATI ³	p-xylene	135-155°/3 hr.			17.0	16.9	65.8	66.0	6.7	6.8
(Et ₂ ATI) ₂ Cr	236	Cr(CO) ₆ , ATI ³	p-xylene	125-145°/3 hr.	9.0	9.0	14.5	14.4	68.0	68.8	7.9	7.9
(β ₂ ATI) ₂ Cr	240	Cr(CO) ₆ , ATI	diglyme	140°/4 hr. ²	6.0	5.8	9.7	9.5	79.0	78.7	5.2	5.3
(Me ₂ ATI) ₂ Mo	308°dec.	Mo(acac) ₃ , ATI	diglyme	145-170°/4 hr.	17.8	18.0	15.6	15.3	60.5	60.1	6.2	6.2
(acac)(Me ₂ ATI) ₂ Mo	272	Mo(acac) ₃ , ATI	diglyme	145-160°/1.5 hr.	19.6	19.4	11.4	11.4	56.4	55.9	6.0	6.0
(Me ₂ ATI) ₂ Mn	262	Mn ₂ (CO) ₁₀ , ATI ⁴	p-xylene	130-140°/4 hr.	11.1	11.3	16.9	17.2	65.4	65.6	6.7	6.7
(acac)(β ₂ ATI) ₂ Mn	248	Mn(acac) ₃ , ATI (1:2)	none	80-140°/1 hr.	7.9	7.8	8.0	7.9	74.2	74.4	5.4	5.5
(acac)(pT ₂ ATI) ₂ Mn		Mn(acac) ₃ , ATI (1:2)	none	80-140°/1 hr.								
(acac) ₂ (Et ₂ ATI)Mn	164	Mn(acac) ₃ , ATI (1:1)	p-xylene	85°/0.5 hr.	12.8	12.8	6.5	6.5	58.9	59.1	6.8	6.8
(acac) ₂ (β ₂ ATI)Mn	146	Mn(acac) ₃ , ATI (1:1)	p-xylene	85°/0.5 hr.	10.5	10.3	5.3	5.3	66.5	67.1	5.0	5.8
(Me ₂ ATI) ₂ Fe	292	FeCl ₂ , LiATI	THF	30°/2 hr.	11.2	10.7	16.9	17.0	65.3	65.5	6.7	6.8
(acac)(β ₂ ATI) ₂ Fe	267	Fe(acac) ₃ , ATI (1:2)	diglyme	110-115°/3 hr.	8.0	7.7	8.0	7.9	74.1	74.1	5.4	5.4
(acac) ₂ (Et ₂ ATI)Fe	136	Fe(acac) ₃ , ATI (1:1.1)	diglyme	110-115°/2 hr.	13.0	13.2	6.5	6.8	58.6	58.5	6.8	6.9
(Et ₂ ATI) ₂ Mn	145	Mn ₂ (CO) ₁₀ , ATI ⁴	p-xylene	152°/2 hr.	13.5	13.2	13.8	13.6	65.1	65.4	7.5	7.5
(pT ₂ ATI) ₂ Mn	258	Mn ₂ (CO) ₁₀ , ATI ⁴	p-xylene	152-162°/5 hr.			8.6	8.8	77.2	77.7	5.8	6.0
(Et ₂ ATI) ₂ Fe	144	FeCl ₂ , LiATI	THF	30°/2 hr.	13.7	13.4	13.8	13.5	65.0	64.7	7.4	7.2
(Et ₂ ATI) ₂ Co	140	CoCl ₂ , NH ₃ , ATI	CHCl ₃ /CH ₃ OH	reflux, 20 min.	14.4	14.3	13.7	13.7	64.5	64.3	7.4	7.4
(β ₂ ATI) ₂ Co	231	CoCl ₂ , NH ₃ , ATI	CHCl ₃ /CH ₃ OH	reflux, 20 min.	9.8	9.5	9.3	9.2	75.8	76.8	5.0	5.0
(pT ₂ ATI) ₂ Co	302	CoCl ₂ , NH ₃ , ATI	CHCl ₃ /CH ₃ OH	reflux, 20 min.	8.9	8.9	8.5	8.8	76.7	77.3	5.8	6.0
(acac)(β ₂ ATI)Ni	212	Ni(acac) ₂ , ATI (1:1.1)	diglyme	110°/1 hr.	13.7	13.3	6.5	7.0	67.2	66.9	5.0	5.1
(β ₂ ATI) ₂ Pd	333	Pd(acac) ₂ , ATI (1:2.2)	diglyme	110-120°/5 hr.	16.4	16.3	8.6	8.3	70.3	70.0	4.7	4.5
(acac)(β ₂ ATI)Pd	221	Pd(acac) ₂ , ATI (1:1.1)	diglyme	110-115°/1 hr.								
(acac)(pT ₂ ATI)VO	226	VO(acac) ₂ , ATI (1:1.25)	none	105-110°/2.5 hr.	11.0	10.9	6.0	6.2	67.0	67.2	5.6	5.6

(1) Measured in sealed tubes.

(2) In Carius tube.

(3) Also prepared by reaction of anhydrous CrCl₂ with lithio derivative of ATI in THF at room temperature.(4) Also prepared by reaction (a) of anhydrous MnCl₂ with lithio derivative of ATI in THF at room temperature, and (b) of Mn(acac)₃ and Me₂ATI (molar ratio of 1:4.5) at 80-140°/1.5 hr.

sample and by analyses. The small amount of mixed chelate obtained in the reaction was not isolated.

Preparation of (acac)₂((C₂H₅)₂ATI)V^{III}.—A mixture of 8.2 g (0.0466 mol) of (C₂H₅)₂ATI and 5.46 g (0.0156 mol) of V(acac)₃ was heated with stirring at 110° until a complete solution was obtained. The solution was then heated under the distillation conditions: 105-110° (4 mm) for 80 min; 115° (4 mm) for 30 min. Pentane (35 ml) was added into the viscous reaction product, and the black powder obtained after standing at 0° for 2 days was recrystallized from ether to give 1.3 g of brown crystals of (acac)₂((C₂H₅)₂ATI)V^{III}.

Preparation of (acac)((C₂H₅)₂ATI)₂V^{III}.—The same amount of starting materials as described for the preceding preparation was heated under the distillation conditions: 105-110° (4 mm) for 30 min; 145-155° (3.5 mm) for 90 min; 155-160° (3.5 mm) for 60 min. The reaction product was then heated at 160° (0.1 mm) to remove excess (C₂H₅)₂ATI. The reaction product was extracted with 25 ml of refluxing heptane. The 6.4 g of crude product obtained from this extract was recrystallized from ether to give 1.5 g of black crystals of (acac)((C₂H₅)₂ATI)₂V^{III}.

Nmr Results and Discussion

The observed resonance frequencies of the chelates examined are presented in Table I. As indicated above, the assignments are not entirely unambiguous.

The widths of the lines varied from 20-30 to 200-300 cps so that in no case was it possible to observe nuclear spin-spin structure. This situation may be contrasted to that in the nickel(II) aminotroponimines discussed previously. The assignments are based principally on comparisons between complexes with different N substituents. Thus it is assumed that, on passing from the N,N'-dimethyl aminotroponimate to the N,N'-diethyl compound or the N,N'-diphenyl compound, the resonance frequencies of the α, β, and γ protons of the seven-membered ring will be relatively unchanged. Lines not present in all chelates are therefore attributed to protons on the substituent group. Since we are mostly concerned with the spin densities on the seven-membered ring, this procedure provides most of the necessary information. The γ resonance has only half the intensity of the α and β resonances and can be distinguished on this basis. Assignment of the α and β resonances is, strictly speaking, arbitrary and could be reversed. However, as will appear below, there appear to be reasonable theoretical grounds for

believing that in most cases the sign of the α and γ shifts will be opposite that of the β shift, as has been shown unambiguously for the nickel(II) aminotroponiminates, and assignments have been made on this basis.

Our general expectations regarding the interpretation of the contact shifts in this series of aminotroponiminate complexes were based for the most part on earlier results on a corresponding series of acetylacetonates.² In this case it was found that for the earlier transition metals the predominant spin-delocalizing mechanism involved charge transfer from the metal ion to the bottom antibonding π ligand orbital. For the later transition metals an additional contribution involving charge transfer from the top bonding ligand π orbital to the metal d orbitals was also postulated. The aminotroponiminate ligand differs from the acetylacetonate ligand in that the top bonding π orbital is considerably higher in energy ($+0.3808\beta$ compared to $+0.9417\beta$ on a simple Hückel calculation)⁸ and should therefore be much more favorable for ligand-to-metal charge-transfer interaction. Consistent with this we have previously shown that the nickel(II) aminotroponiminate spectra can be interpreted in considerable detail on the assumption that this is the only significant spin-delocalizing mechanism. We therefore anticipated that the behavior of the aminotroponiminate series would be complementary to that of the acetylacetonate series; namely, for the later transition metals ligand-to-metal charge transfer would dominate but for the earlier members of the series we might find some evidence for an additional contribution from a metal-to-ligand charge-transfer process.

The over-all results of Table I are consistent with this picture, but the details fit less satisfactorily than for the acetylacetonates. Thus the expected pattern for the distribution of positive spin in the top bonding ligand π orbital leads to high-field shifts for the α and γ protons and a low-field shift for the β protons. This pattern is maintained from d^8 Ni(II) through d^4 Mn(III). At d^3 Cr(III) the β shift becomes much smaller, and at d^2 V(III) it becomes positive. A further competitive mechanism is therefore indicated for the early transition metals.

The predominance of the ligand-to-metal π charge-transfer mechanism for the later transition metals seems clear. The results for the earlier transition metal ions are, however, more difficult to interpret since several factors could be involved. Thus for the ions with a less than half-filled d shell the donation of positive spin to the metal leaving negative (β) spin on the ligand is a possibility. This would reverse the expected contact shifts. As indicated above metal-to-ligand charge transfer is also feasible. A simple Hückel MO calculation⁸ gives the bottom antibonding π orbital an energy of -0.6662β which is very little higher than that of the corresponding acetylacetonate orbital (-0.6103β).

(8) Parameters used in Hückel calculations: $\alpha(\text{C}) = \alpha$, $\alpha(\text{=O}) = \alpha + 2\beta$, $\alpha(\text{-N=}) = \alpha + \beta$, $\alpha(\text{-O-}) = \alpha + 3.2\beta$, $\alpha(\text{-N-}) = \alpha + 2\beta$, $\beta(\text{CO}) = 1.4\beta$, $\beta(\text{CN}) = 1.2\beta$. See L. E. Orgel, T. L. Cottrell, W. Dick, and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951).

The predicted spin-density distribution in this orbital is $+0.1160$ at the α position, $+0.2613$ at the β position, and 0 at the γ position. Allowing for the effects of spin correlation this leads to the prediction of high-field shifts for the α and β protons and a large low-field shift for the γ proton. The latter prediction in particular is not in accord with the facts. However, there is also a second antibonding π orbital close in energy to the lowest one (-0.7021β compared to -0.6662β). This orbital is symmetric with respect to reflection in the plane of the ligand whereas the lowest antibonding orbital is antisymmetric, but both can interact with the d orbitals. Furthermore, it has a larger coefficient for the N p orbital so that stronger interaction is predicted. Spin density in this orbital will lead to a high-field shift for the α and γ protons and a low-field shift for the β proton. In addition to this we cannot eliminate the possibility of spin reaching in the σ system of the ligand either by direct transferal or by a polarization mechanism. It is apparent that, although no single mechanism can account for the observed shifts in the aminotroponiminates of the early transition metals, a suitable combination could account for virtually any pattern. At present we do not feel justified in speculating on the nature of this combination since to do so meaningfully would require more reliable and elaborate calculations than we have undertaken.

The mixed acetylacetonate-aminotroponiminate chelates of V(III) and Mn(III) are of particular interest. We have previously demonstrated in the nickel(II) aminotroponiminate system the competitive nature of the π bonding to different ligands. The mixed V(III) chelates of acetylacetonate and hexafluoroacetylacetonate show rather different behavior. In both of these cases the comparison was between ligands with qualitatively the same but quantitatively different π -bonding characteristics. However, aminotroponiminate and acetylacetonate have qualitatively different π -bonding characteristics, and it was of interest to investigate how this factor would be manifested in the contact shifts. The results are particularly striking for the mixed V(III) complexes. Considering first the aminotroponiminate shifts, the introduction of one acetylacetonate ligand has a relatively minor effect on the aminotroponiminate shifts. However, substitution of the second acetylacetonate changes the aminotroponiminate pattern drastically, leading to low-field shifts for the α and γ protons and a high-field shift for the β proton. This is the pattern we would expect for *negative* spin density delocalized in the top bonding orbital. Conversely, if we consider the acetylacetonate shifts, the substitution of one aminotroponiminate does not substantially change the pattern from that shown by vanadium(III) tris(acetylacetonate). Some splitting of the CH_3 resonance is apparent, but this is to be expected since the methyl groups are no longer equivalent. However, substitution of two aminotroponiminates changes the CH resonance from high field to low field. This is similar to the shift

observed in iron(III) acetylacetonate which has been interpreted as resulting from the donation of a *negative* spin to the half-filled d shell leaving *positive* spin on the ligand.

Insofar as the contact shifts reflect the π -bonding properties of the complex, which they do if our earlier interpretations are correct, these results demonstrate the effect of a given ligand on the bonding properties of another ligand. It is just this kind of interaction which must be responsible for the specificity of certain transition metal complexes in homogeneously catalyzed reactions. Thus only the right combination of ligands on a given transition metal ion will provide the optimum bonding conditions for the substrate in a homogeneously catalyzed reaction. The detailed interpretation of the present results must await a more rigorous theoretical treatment of the type previously attempted for vanadium(III) acetylacetonates. However, one or two preliminary observations can be made at this point. The d^2 V(III) ion has one empty and two half-filled d orbitals which are available for π bonding even in strictly octahedral symmetry. In the complex with one aminotroponimine and two acetylacetonate ligands the negative spin on the aminotroponimate indicates that this ligand is interacting with the empty d orbital since this is the only orbital which can accept a positive spin leaving negative spin on the ligand. On the other hand, in the complex with one acetylacetonate and two aminotroponimines it appears that the acetylacetonate is interacting with a half-filled orbital since positive spin is delocalized. This result can perhaps be rationalized if it is remembered that the metal-to-ligand charge-transfer interaction can only profitably involve a half-filled

orbital; if the d orbital is empty, such interaction can lend neither to a gain in energy nor to observable contact shifts. Since metal-to-ligand π charge transfer is thought to be the most important interaction with the acetylacetonate ligand, it therefore seems plausible that this ligand will prefer to interact with a half-filled orbital. With aminotroponimine, on the other hand, since only ligand-to-metal π charge transfer need be considered, the preference could well be for interaction with an empty d orbital, donating an α electron to keep parallel spins in the d orbitals as much as possible and maximize the energy in this way. It is perhaps plausible that these preferences should only become apparent when there is only one ligand of a given type since with two or more identical ligands there may well be interactions with both filled and half-filled orbitals, and the over-all shifts will represent a combination of effects.

Turning to the mixed Mn(III) chelates, some fairly substantial changes are again apparent in the shifts of the mixed chelates. However, there is no drastic change in the pattern as there is for the V(III) complexes. If the π interactions are predominantly with those d orbitals available for π bonding even in octahedral symmetry, this result is understandable since all such orbitals are half-filled. It is interesting to note that in the mixed chelates some of the aminotroponimate resonances are split, reflecting the expected nonequivalence of these protons in the lower symmetry.

Finally, it should be noted that the susceptibility measurements indicate that the tris aminotroponimates of both Mn(III) and Fe(III) are low-spin complexes, whereas the tris acetylacetonates and the mixed complexes are high spin.

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Lanthanide and Actinide Complexes of Glycine. Determination of Stability Constants and Thermodynamic Parameters by a Solvent Extraction Method

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The first stability constants of the complexes formed between glycine and trivalent Ce, Pm, Eu, Am, and Cm at an ionic strength of 2.0 *M* (NaClO₄) have been determined by a solvent extraction technique. Under the conditions of the experiments (pH 3.64) complexation takes place between the metal cation and the zwitterion NH₃⁺CH₂CO₂⁻ while complexation by the free anion to form a chelate is negligible. Values for enthalpy and entropy for the formation of the monoligand complex have been determined by a temperature differential method. In all cases the enthalpy of complexation is endothermic, the complexes being stabilized by a relatively large positive entropy change. This indicates the formation of inner-sphere complexes similar to those formed between lanthanide and actinide ions and simple carboxylate ligands.

Introduction

In an earlier study of the complexation of light lanthanides by glycine and β -alanine, it was assumed that the ligand anion formed a chelate with the cation.¹

(1) M. Cefola, A. S. Tampa, A. V. Celiano, and P. S. Gentile, *Inorg. Chem.*, **1**, 290 (1962).

Preliminary investigations² using the method of pH titration raised serious doubts about this interpretation of the results. We have used a solvent extraction technique at constant pH to restudy the complexing by glycine. This ligand can exist in three forms

(2) J. L. Bear and G. R. Choppin, unpublished data, 1963.