TABLE III

SELECTED INFRARED FREQUENCIES (cm^{-1}) AND ASSIGNMENTS FOR DIBENZYL SULFOXIDE, ACETONE (A), $M((bz)_2SO)_4A_2^{2+}$, AND $Cu((bz)_2SO)_4^{2+}$[a–c]

$(bz)_2SO$ (L)	Acetone (A)	$MnL_4A_2^{2+}$	$FeL_4A_2^{2+}$	$CoL_4A_2^{2+}$	$NiL_4A_2^{2+}$	$ZnL_4A_2^{2+}$	$CuL_4A_2^{2+}$	CuL_4^{2+}	Assignments
	530 s[d]	556 s	556 s	558 s	556 m	557 m	562 m		δ_{CO}(acetone)
		535 s	533 s	540 m	544 m	537 m	535 s		
473 s		476 s	477 s	474 s	476 s	478 s	483 s	487 s	$\delta_{CSO}((bz)_2SO)$
		(465)	(468)	468 m	(468)	(468)	(471)	(470)	
	385 w[d]	381 s	383 s	385 s	384 s	383 s	388 s		δ_{CCC}(acetone)
372 m								360 m	
(360)									
331 m		(347)	348 m	(349)			347 m	(353)	$\delta_{CSO}((bz)_2SO)$
			340 m	(344)	(343)	(346)		(348)	
		339 s	334 m	340 s	338 s	335 s	334 m	324 s	
							305 w		
							301 w		
			(283)		285 w	(287)		289 w	
		277 m, br	278 w	281 m, br	276 w	280 m			
						(273)			
			(250)		257 w	253 m			
		245 m	245 w	249 m		248 m			
		~200 s	211 s	219 m	226 s, br	209 m	263 s	265 m	ν_{M-O}

[a] Abbreviations: L and $(bz)_2SO$, dibenzyl sulfoxide; A, acetone; s, strong; m, medium; w, weak; br, broad; parentheses signify a shoulder. [b] Nujol mulls. [c] ClO_4^- is the anion in all cases. [d] Reference 13.

containing complexes is undoubtedly due to a static Jahn–Teller distortion, as evidenced by the low 26-cm^{-1} $\Delta\nu_{C-O}$ value in $Cu((bz)_2SO)_4(CH_3C(O)CH_3)_2^{2+}$. In this complex the weakly held axial acetone allows stronger in-plane bonding than in the other acetone-containing complexes. Similar behavior is observed for $Cu((C_6H_5)_2SO)_4(CH_3C(O)CH_3)_2^{2+}$ and $Cu((C_6H_5)_2SO)_6^{2+}$, where the ligand is diphenyl sulfoxide.[11]

The dibenzyl sulfoxide infrared assignments in Table II are based on Green's study[12] of diphenyl sulfoxide to which he assigned CSO bending fundamentals at 481 and 303 cm^{-1}. By analogy the 473- and 331-cm^{-1} bands in dibenzyl sulfoxide and the bands in the complexes in the same region are also assigned to the CSO deformations. As in $Cd((C_6H_5)_2SO)_2I_2$ studied by Green, the frequency of both deformations increases upon complex formation. The CO bending fundamental in acetone[13] occurs at 530 cm^{-1}, but in the complexes this mode results in strong higher frequency bands near 558 and 540 cm^{-1}. The weak CCC deformation at 385 cm^{-1} is assigned to the strong band near 384 cm^{-1} in the complexes. A third acetone fundamental, the weak out-of-plane skeletal vibration at 484 cm^{-1}, is not observed in the complexes owing to the predominant δ_{CSO} near 478 cm^{-1}.

The assignment of ν_{M-O} in the dibenzyl sulfoxide series is difficult because of the large number of aromatic vibrations below 600 cm^{-1} (Figure 1). Several relationships may be considered in the attempt to assign ν_{M-O} in the dibenzyl sulfoxide complexes. (1) As the mass of the ligand increases, ν_{M-O} decreases. Thus ν_{M-O} should be lower than the 325-cm^{-1} frequency found in analogous pyridine N-oxide complexes.[14] (2) The usual metal order of frequency, Ni(II) > Co(II) > Fe(II) > Mn(II), should be observed. (3) As the coordination number of the complex with the same ligand decreases, ν_{M-O} increases. For example, ν_{M-O} for CuL_4^{2+} is about 50 cm^{-1} higher than that for the NiL_6^{2+} analog when L is tetramethylene sulfoxide[10] or dimethyl sulfoxide.[1,15] The series of bands (Figure 1, Table III) which best fulfills the criteria is found in the $M((bz)_2SO)_4(CH_3C(O)CH_3)_2^{2+}$ series at 263 cm^{-1} for Cu(II) and near 220 cm^{-1} for other M(II), and in $Cu((bz)_2SO)_4^{2+}$ at 265 cm^{-1}.

Acknowledgment.—The preparation of Figure 1 by Anne C. Weber is appreciated. This research was supported in part by the Central University Research Fund, Grant No. 358.

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(11) P. W. N. M. Van Leeuwen, *Rec. Trav. Chim.*, **86**, 201 (1967).

(12) J. H. S. Green, *Spectrochim. Acta*, **24A**, 1627 (1968).

(13) G. Dellepiane and J. Overend, *ibid.*, **22**, 593 (1966).

(14) Y. Kakiuti, S. Kida, and J. V. Quagliano, *ibid.*, **19**, 201 (1963).

(15) J. H. Weber, *Inorg. Nucl. Chem. Letters*, in press.

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Protonation of Carbonyl Groups in Aminocarboxylate Coordination Compounds

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There has been considerable study[1] of protonation of carbonyl groups in aliphatic ketones, aldehydes, carboxylic acids, esters, anhydrides, and simple amides. Recently we reported on the protonation of carbonyl groups in peptides and amino acids.[2] Now we wish to report that carbonyl groups in certain aminocarboxylate coordination compounds are protonated in FSO_3H–

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(1) See references quoted in ref 2.

(2) J. L. Sudmeier and K. E. Schwartz, *Chem. Commun.*, 1646 (1968).

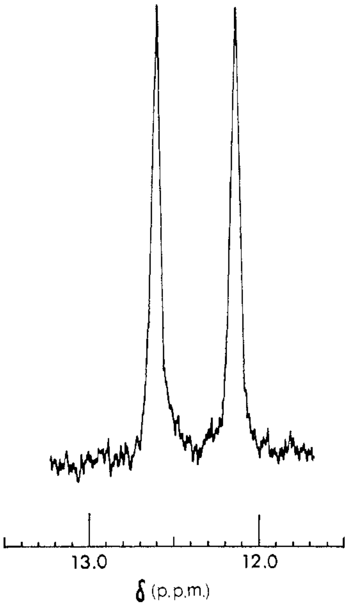

Figure 1.—Partial 100-MHz nmr spectrum of Co^{III}EDTA in FSO_3H–SbF_5–SO_2 at −80°.

SbF_5–SO_2 (super acid) at approximately −80° without decomposition and that the C=OH protons are readily observed by nuclear magnetic resonance (nmr). Rapid identification of the relative numbers of carbonyl groups in different magnetic environments is an obvious application of this phenomenon and should prove useful for identifying various structural isomers of coordination compounds. The chemical shifts of C=OH protons which we have observed in these compounds are in the range 11–14 ppm *vs.* tetramethylsilane (TMS)—a range in which there are few possible interferences.

In Co^{III}EDTA[3] there is a pair of in-plane ("G ring") carbonyl groups and a pair of out-of-plane ("R ring") carbonyl groups, and the pairs are related by a C_2 axis. As shown in Figure 1, the nmr spectrum of Co^{III}EDTA in super acid exhibits well-separated peaks of equal intensities at 12.09 and 12.56 ppm *vs.* TMS. This result would be expected if all carbonyl groups were protonated as shown in the tripositive cation I. This species represents a stable form of the transient intermediate first proposed by Terrill and Reilley for acid-catalyzed deuteration of α-hydrogen atoms.[4] Similar results are obtained for Co^{III}CyDTA[5] (see Table I). There has been no evidence to date of the relative abundance of *cis* and *trans* isomers about the C=O bond in these protonated species.

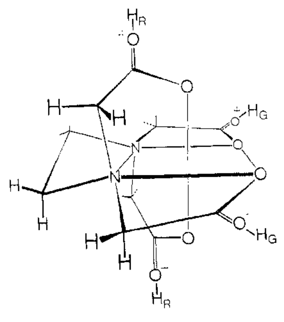

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TABLE I

CHEMICAL SHIFTS OF C=OH PROTONS IN COORDINATION COMPLEXES IN PPM *vs.* TMS[a]

Compound	Temp, °C[b]	H_R	H_G
Co^{III}EDTA	−80	12.09	12.56
Co^{III}CyDTA	−74	11.94	12.32
trans-Co^{III}(en)EDDA	−90	11.34	...
Co^{III}PDTA	−80	11.96	12.58
trans-Co^{III}(IDA)$_2$[c]	−80	11.76[d]	
Pt^{II}(gly)$_2$	−90	...	13.48

[a] CH_2Cl_2, 5.30 ppm from tetramethylsilane, used as internal standard. [b] Due to variations in temperature calibration, systematic errors of as much as 10° may be expected. The temperature coefficient of the C=OH proton chemical shifts indicates that systematic errors of as much as 0.05 ppm may be expected. [c] IDA = iminodiacetic acid; *trans*-Na[Co^{III}(IDA)$_2$]·$2H_2O$ was prepared by the method of J. Hidaka, Y. Shimura, and R. Tsuchida, *Bull. Chem. Soc. Japan*, **35**, 567 (1962). [d] The designations H_R and H_G are undefined for *trans*-Co^{III}(IDA)$_2$, because in this centrosymmetric molecule (point group C_{2h}) all carbonyl groups are equivalent.

The nmr spectrum of *trans*-Co^{III}(en)EDDA[6] in super acid displays a single peak in the carbonyl region at 11.34 ppm. Because *trans*-Co^{III}(en)EDDA has only out-of-plane carbonyl groups, the observation of a single peak supports the interpretation given for the Co^{III}EDTA spectrum. The smaller chemical shift of H_R in the case of *trans*-Co^{III}(en)EDDA favors the assignment in which the peaks of smaller chemical shift represent H_R for Co^{III}EDTA and its analogs.

Co^{III}PDTA[7] has no C_2 axis and, therefore, has four nonequivalent carbonyl groups. The carbonyl region of the spectrum of Co^{III}PDTA in super acid shows only two peaks of equal intensities at 11.96 and 12.58 ppm, probably because of the remoteness of the asymmetric site.

The upfield portions of the spectra for the Co^{III} complexes reported herein bear a close resemblance to the corresponding spectra in common solvents, *e.g.*, water, although the line widths are greater in the more viscous super acid medium. Absence of change in color or appearance of the complexes supplies additional evidence that they remain intact in super acid. The N–H protons in *trans*-Co^{III}(en)EDDA and *trans*-Co^{III}(IDA)$_2$ appear as a single broad resonance at ~6.15 ppm.

Although greater certainty in the assignments must await further study, the use of super acid sometimes allows rapid, simple determination of the number of

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[3] EDTA = ethylenediaminetetraacetic acid; K[Co^{III}EDTA]·H_2O was prepared by the method of F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **83**, 2610 (1961).

[4] J. B. Terrill and C. N. Reilley, *Inorg. Chem.*, **5**, 1988 (1966).

[5] CyDTA = cyclohexanediaminetetraacetic acid; K[Co^{III}CyDTA]·$3H_2O$ was prepared by the method of F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **83**, 2610 (1961).

[6] EDDA = ethylenediaminediacetic acid; *trans*-[Co^{III}(en)EDDA]NO_3 was prepared by the method of J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **4**, 1576 (1965).

[7] PDTA = propylenediaminetetraacetic acid: K[Co^{III}PDTA]·H_2O was prepared by the method of F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **83**, 2610 (1961).

different kinds of carbonyl groups, which gives promise for its use in coordination chemistry. Another important advantage of the method is that super acid can protonate and, therefore, solubilize many neutrally charged compounds which are so insoluble in ordinary solvents that observation by nmr is virtually impossible. For example, $Pt^{II}(gly)_2$,[8] which is sparingly soluble in such solvents as chloroform, water, and dimethyl sulfoxide, dissolves readily in super acid, yielding a broad carbonyl region nmr pattern centered at 13.48 ppm.

It appears that this technique is limited to kinetically inert compounds, because EDTA chelates of Mg^{2+}, Ca^{2+}, and Pb^{2+} yield no discernible resonance in the 11–14-ppm range, probably because of their complete dissociation in super acid.

[8] L. M. Volshtein and G. G. Motyagina, *Russ. J. Inorg. Chem.*, **5**, 840 (1960).

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Manganese Nuclear Magnetic Resonance of the Phosphorus Trifluoride Derivatives of Manganese Pentacarbonyl Hydride

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We have studied the ^{55}Mn nuclear resonances for the series of compounds $HMn(CO)_{5-x}(PF_3)_x$, $x = 0–5$, previously reported by Miles and Clark.[1] Resonances were obtained for the pure liquids in 5-mm evacuated nmr tubes using a Varian broad-line nmr spectrometer with a fixed-frequency 10-MHz radiofrequency unit. Magnetic field calibrations were obtained with an Alpha proton nmr magnetometer and a Hewlett-Packard 5246L frequency counter. Only a single manganese resonance was observed for each composition even though geometric isomers are present. For the intermediate compositions $x = 1–4$, more than one isomer is seen by ^{19}F and ^{1}H nmr (as separate resonances) and by infrared spectroscopy.[2] It is estimated that minor isomers can constitute 15–20% of each composition. This suggests that the isomers for the intermediate species have chemical shifts which differ by less than the line widths (200 ppm). No unusual line-width behavior was observed which could be attributed to the presence of isomers. This agrees with the observation of only a single broad resonance for a mixture of *cis*- and *trans*-$CH_3COMn(CO)_4(P[C_6H_5]_3)$.[3] In addition, there was no fine structure nor line-width trends that could be attributed to manganese–phosphorus coupling.

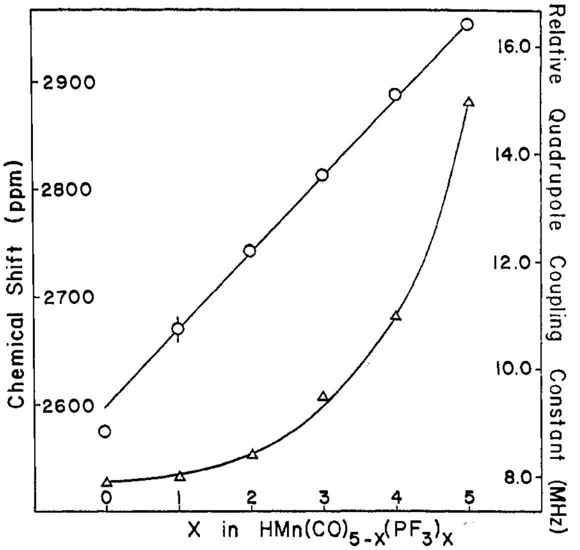

Figure 1.—The ^{55}Mn chemical shift (O) within the series $HMn(CO)_{5-x}(PF_3)_x$ and the relative quadrupole coupling constants (Δ) for the same series. The error bar of the chemical shift is shown for $HMn(CO)_4(PF_3)$ and is the same for the other members of the series.

The chemical shifts observed for this series of compounds, shown in Table I and Figure 1, are larger upfield (diamagnetic) shifts than previously observed for manganese.[3] This is to be expected, however, because substitution of PF_3 for CO also causes blue shifts in the optical spectra[4] of most $M(CO)_x(PF_3)_y$ systems. The blue shift has actually been observed by comparing the spectra of five of the manganese–hydride species. These increased electronic splittings attenuate the orbital mixing that leads to paramagnetic shifts such as those observed for cobalt(III) complexes.[5] It is also possible that diamagnetic susceptibility effects are important for these complexes which have very little paramagnetism. The trend of the diamagnetic contributions should be in the same direction as the paramagnetic terms in this series because the

TABLE I

NMR DATA FOR $HMn(CO)_{5-x}(PF_3)_x$

x	$\sigma(^{55}Mn)$,[a,b] ppm	Line width,[c] G	Rotational correlation time,[d] τ_0, nsec	e^2qQ/h,[d] MHz	$\sigma(H)$,[e] ppm
0	2578	2.28	0.22	7.9	38.7
1	2673	2.35	0.22	8.0	39.9
2	2742	2.21	0.19	8.4	41.8
3	2813	2.35	0.16	9.5	...
4	2888	3.20	0.16	11.0	...
5	2953	5.93	0.16	15.0	...

[a] Relative to saturated aqueous $LiMnO_4$ without bulk susceptibility corrections. [b] Estimated error ±10 ppm. [c] Derivative peak to valley line widths at 30°; estimated error ±0.05 G. [d] Estimated as described in text. [e] Absolute.

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[1] W. J. Miles, Jr., and R. J. Clark, *Inorg. Chem.*, **7**, 1801 (1968).

[2] W. J. Miles, Jr., and R. J. Clark, to be submitted for publication.

[3] F. Calderazzo, E. A. C. Lucken, and D. F. Williams, *J. Chem. Soc.*, *A*, 154 (1967).

[4] A. K. Wensky and R. J. Clark, unpublished work; R. J. Clark, *Inorg. Chem.*, **6**, 299 (1967).

[5] J. S. Griffith and L. E. Orgel, *Trans. Faraday Soc.*, **53**, 601 (1957); R. Freeman, G. R. Murray, and R. E Richards, *Proc. Roy. Soc.* (London), **A242**, 455 (1957).