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Infrared Spectra of Linear and Nonlinear Transition-Metal Nitrosyls.[1] 2. Dimethyldithiocarbamate and *o*-Phenylenebis(dimethylarsine) Complexes of $\{FeNO\}^6$, $\{FeNO\}^7$, and $\{CoNO\}^8$

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The infrared spectra of linear and strongly bent metal–nitrosyl complexes have been obtained from 33 to 4000 cm^{-1}. The compounds studied include *cis*-$[Fe(NO)(S_2CN(CH_3)_2)_2I]$, $Fe(NO)(S_2CN(CH_3)_2)_2$, $Co(NO)(S_2CN(CH_3)_2)_2$, *trans*-$[Fe(NO)((As(CH_3)_2)_2C_6H_4)_2(NCS)][ClO_4]_2$, *trans*-$[Fe(NO)((As(CH_3)_2)_2C_6H_4)_2Br]ClO_4$, $[Co(NO)((As(CH_3)_2)_2C_6H_4)_2][ClO_4]_2$, *trans*-$[Co(NO)((As(CH_3)_2)_2C_6H_4)_2Br]ClO_4$, and their ^{15}N-substituted derivatives. The skeletal vibrations of these $\{MNO\}^n$ groups have been identified and force constants derived from the three-body model. These results show that the simple three-body model has a wide range of applicability for defining the vibrations of the MNO group, even in complexes with low symmetry and with other light atoms in the coordination sphere.

Introduction

Infrared spectroscopy is of proven value for identifying and characterizing transition-metal complexes of NO. Most attention has been focused on the NO stretching vibration because of its prominence in the infrared spectrum.[2] Although it is now widely recognized that ν_{NO} alone cannot distinguish linear MNO geometry from bent MNO geometry,[3-6] the more complete studies of infrared spectra of metal–nitrosyl complexes which have appeared in recent years still offered some promise for obtaining reliable information about both the geometry and bonding of the MNO group.[1,7-9] However, an examination of the literature shows that most normal-coordinate analyses of metal nitrosyls have dealt with complexes containing linear or nearly linear MNO groups. Those few strongly bent complexes which have been studied previously either were not well-characterized structurally or had chemical or physical properties which prevented complete analysis of their IR spectra. Since the vibrations of linear mononitrosyl complexes can be closely approximated by the general valence force field of a triatomic species[1,7-9] and the geometry and electronic properties of both linear and bent $\{MNO\}^n$ groups can be described by treating them as covalent triatomic species,[10-12] the following study of the skeletal vibrations of strongly bent MNO complexes which have been structurally characterized[13-15] was undertaken to explore the range of applicability of the three-body model to strongly bent MNO groups.

Experimental Section

The preparation and analyses of the dimethyldithiocarbamate (DMDTC) complexes used in these studies are reported elsewhere.[16] The preparations of *o*-phenylenebis(dimethylarsine) (DAS) complexes with ^{14}NO were described previously[4,17] while the ^{15}NO derivatives were prepared from ^{15}NO (Bio-Rad, 95%) using similar methods. All spectra were recorded several times using samples of different concentrations in KBr disks, KI disks, and Nujol mulls on polyethylene pellets (Tables I and II). The IR spectra from 33 to 400 cm^{-1} were recorded on a Beckman IR-11 spectrophotometer equipped with a germanium bolometer detector[18] cooled to 4.2 K. The spectral region from 200 to 4000 cm^{-1} was measured on a Beckman IR-12 spectrophotometer. The spectral region from 33 to 350 cm^{-1} was calibrated using the water bands at 208.5 and 253.9 cm^{-1}, and the region from 350 to 4000 cm^{-1} was calibrated with the polystyrene bands at 906.5, 1027.7, 1154.0, 1601.0, 1943.5, 2849.9, and 3026.3 cm^{-1}. A du Pont Model 310 curve resolver was used to separate overlapping peaks. The estimated errors in the peak positions are ±1 cm^{-1} for the raw data and ±2 cm^{-1} for the curve-resolved data. Discrepancies between these data and those reported by others for the same compounds mainly occur with overlapping bands. Other minor discrepancies were attributed to differences in calibration standards.

The force constants were obtained by matching the observed and calculated frequencies using a local modification of NORCRD.[19] This program was tested by duplicating the calculations of Herzberg[20] for the frequencies of H_2O, CO_2, and CS_2. The bond distances and angles used in obtaining the force constants for these complexes are set out in Table III. The parameters in Table III correspond to those obtained directly from the structural studies[13-15,21] or in a few cases to those of closely analogous compounds.[16,22] Since the force constants are relatively insensitive to the structural parameters, closely related analogues provided satisfactory internal coordinates.

Results

A. Infrared Spectra. Complete IR spectra were obtained between 33 and 4000 cm^{-1}. The skeletal vibrations of the MNO groups are found in two distinct regions: 1500–2000 cm^{-1} (ν_{NO}) and below 650 cm^{-1} (ν_{MN} and δ_{MNO}). Each of the compounds in Tables I and II exhibits at least one very strong band above 1500 cm^{-1} which shifts by 25–37 cm^{-1} upon ^{15}N substitution. These strong bands, identified as ν_{NO}, are usually very broad and frequently have shoulders or are split by as much as 30 cm^{-1}.

Identification of ν_{MN} and δ_{MNO} presents several difficulties which partially accounts for the small number of these vibrations which have been reported in the literature. Both ν_{MN} and δ_{MNO} are relatively weak and occur below 650 cm^{-1}, a region which has many strong bands from the other ligands in the complex. In linear MNO complexes, the degenerate bending vibration, δ_{MNO}, is usually more intense than ν_{MN}, has a larger ^{15}N isotopic shift (10–15 cm^{-1}), and frequently has its degeneracy lifted by molecular symmetry or by solid-state effects. The M–N stretch of linear complexes is usually weak and has only a small ^{15}N isotopic shift (2–6 cm^{-1}). These properties make it the most difficult band to identify in linear MNO complexes. In strongly bent MNO complexes, the relationship between ν_{MN} and δ_{MNO} is modified: the intensity of ν_{MN} is increased, the intensity of δ_{MNO} is diminished, and only one bending vibration is expected because δ is nondegenerate in strongly bent MNO groups. The main difficulties encountered in identifying the skeletal vibrations of the MNO groups are caused by interference of the bands of the other ligands in the complex. Consequently the DAS, DMDTC (DMDTC is dimethyldithiocarbamate), and en (en is ethylenediamine) complexes will be discussed separately below.

DMDTC Complexes. The DMDTC ligand has a relatively uncomplicated IR spectrum consisting of one group of intense bands between 1550 and 900 cm^{-1} and another group of bands of medium intensity near 400 cm^{-1}. The intense band near 1550 cm^{-1} and the band of medium intensity near 370 cm^{-1} are known to be sensitive to the metal to which DMDTC is coordinated. The sensitivity of the DMDTC bands in the 300-cm^{-1} region to the attached metal made the identification of ν_{MN} and δ_{MNO} difficult.

Several papers have reported the IR spectra of dithiocarbamates,[23] but reasonably complete normal-coordinate analyses and band assignments have been carried out only

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Table I. Infrared Spectra (cm^{-1}) of the $\{MNO\}^n$ Derivatives of Dimethyldithiocarbamate

$Fe(NO)(DMDTC)_2$		$Fe(NO)(DMDTC)_2I$		$Co(NO)(DMDTC)_2$		
^{14}N	^{15}N	^{14}N	^{15}N	^{14}N	^{15}N	assign
46 sh[a]	43 sh					*c*
				55	55	
89	89	74	74	92	92	ν_{30}[b]
106 w	102					*c*
147	148	127	124(?)	151	151	
192	193	214 w		189 vvw	189 vvw	ν_{17}
235	235					
				248	248	
				254	254	
263	263	261	260	259	259	ν_{16}
285	282					
				315	312	*c*
360	360	366	365	373		ν_{28}
370	371					ν_{10}
414	414	408	410	412	414	ν_{27}
443	442	442	442	442	442	ν_9
	478 vw	461				
544 vw						
		542	530			*c*
		550	546			*c*
554	554			551	551	ν_{15}
563	559	565	551			*c*
				556	557	
575	575	584	584	578	578	ν_8
		621	617			*c*
		752				
978	978	980	980	982	982	ν_{26}
1020	1020	990	990			
1048	1048	1048	1048	1051	1051	ν_{25}
1110					1110	
1150	1150	1155	1154	1147	1150 (60 sh)	ν_{14}
1248	1248	1250	1250	1250	1250	ν_{24}
1395	1395	1395	1394	1397	1395	ν_5, ν_{23}
			1400	1406 sh	1406 sh	ν_5, ν_{23}
1450	1450			1445 w	1445 w	$\nu_4, \nu_{13}, \nu_{22}$
1535	1535	1544	1543	1540	1540	ν_3
1692	1655			1626	1594	*c*
		1812	1772			*c*
		1830	1794			*c*

[a] sh = shoulder, w = weak, m = medium, s = strong, v = very, br = broad. [b] Reference 25. [c] MNO skeletal vibrations; see text for discussion and Table IV for assignments.

recently.[24,25] The position, shape, and relative intensity of many of the IR bands of the dimethyldithiocarbamate ligand are independent of the metal to which they are attached. Consequently, many of the bands listed in Table I were assigned in accordance with those made by Jensen et al.[25] for $Ni(DMDTC)_2$.

The IR spectra of $Fe(NO)(DMDTC)_2$ reported in Table I agree with those of Miki et al.,[26] who observed shifts of only two bands at 1691 and 560 cm^{-1} with ^{15}N substitution. In addition to confirming these frequency shifts, three other bands in the region below 300 cm^{-1} also undergo ^{15}N isotopic shifts. The band at 285 cm^{-1} was observed by Miki,[26] but no ^{15}N frequency shift was reported. The small but reproducible shift of 3 cm^{-1} found for the 285-cm^{-1} band (Table I) is within the estimated error of these experiments (2σ = 4 cm^{-1}). Significant shifts were found for two other bands in this spectral region at 46 and 106 cm^{-1}. The band at 46 cm^{-1} shifted by 3 cm^{-1} and the 106-cm^{-1} band shifted by 4 cm^{-1}. The uncertainty in the position of the band at 46 cm^{-1} is greater than the other isotopic shifts reported because of the polyethylene peak at 66 cm^{-1}. The observed 3- and 4-cm^{-1} shifts for these two bands correspond to the shifts of δ_{FeNO} in linear FeNO groups. It is also possible that one of these two low-frequency bands is associated with other vibrations of the molecule.

Miki et al.[26] also studied the spectra of $Co(^{14}NO)(DMDTC)_2$ and $Co(^{15}NO)(DMDTC)_2$ and reported that three bands shifted with ^{15}N substitution: 1624 → 1596 cm^{-1}, 317 → 311 cm^{-1}, and 259 → 256 cm^{-1}. The present study confirms the shift of ν_{NO} (1626 → 1594 cm^{-1}) and of the nondegenerate bending vibration, δ_{CoNO} (315 → 312 cm^{-1}), but no shift of the band at 259 cm^{-1} was observed. Moreover, this band is present in all of the dithiocarbamate complexes reported here and has been assigned by Jensen et al.[24,25] to a fundamental vibration of the dithiocarbamate ligand (ν_{16}). Although there are three bands in this region (259, 254, 248 cm^{-1}) whose positions are difficult to measure accurately, no reproducible shifts were observed in any of the bands below 260 cm^{-1}. Thus, ν_{CoN} could not be assigned for this complex. In an attempt to identify ν_{CoN} by its small ^{15}N isotopic shift (ca. 1–4 cm^{-1}), $Co(NO)(DEDTC)_2$ (DEDTC is diethyldithiocarbamate) and its ^{15}N derivative were also prepared, but as with the DMDTC derivative, only the bands near 1600 and 320 cm^{-1} were found to shift with ^{15}N substitution.

In contrast with the cobalt complex, a large number of bands (six) were found to shift with ^{15}N substitution of *cis*-$Fe(NO)(DMDTC)_2I$. The two bands observed in the 1800-cm^{-1} region shifted by 36 and 38 cm^{-1} and a total of four bands in the 500–600-cm^{-1} region had ^{15}N isotopic shifts (Figure 1). These six bands were attributed to the three fundamental vibrations of each of two distinct $Fe(NO)(DMDTC)_2I$ species because the relative areas under each pair of bands (ν_{NO}, ν_{FeN}, δ_{FeNO}) have a constant value of 3:2. It is not certain whether these two distinct $Fe(NO)(DMDTC)_2I$ species are the cis and trans isomers or whether two crystallographically distinct lattice sites are occupied by the cis isomer in the crystal. Whatever the origin of these distinct $Fe(NO)(DMDTC)_2I$

Table II. Infrared Spectra (cm^{-1}) of the $\{MNO\}^n$ Derivatives of *o*-Phenylenebis(dimethylarsine)

$[Co(NO)(DAS)_2][ClO_4]_2$		$[Co(NO)(DAS)_2Br][ClO_4]$		$[Fe(NO)(DAS)_2Br][ClO_4]$		$[Fe(NO)(DAS)_2(NCS)][ClO_4]$		
^{14}N	^{15}N	^{14}N	^{15}N	^{14}N	^{15}N	^{14}N	^{15}N	assign
		260 w, sh[a]	260 w, sh					
276	276	273 m	273 m	273	272	275		
357		352	351					ν_{30}
363		362	362	361	361	361	362	ν_{29}, ν_{10}
		371	368					*b*
		378	378	376	375	375	375	ν_{29}, ν_{10}
438	438	440 s	439	440 s	440	440 s	439 s	ν_{19}
				455 w	452	463	458	*b*
458	458			465 w	465	471 w	471 w	δ_{NCS}
476	465							*b*
491	486							*b*
506	494							*b*
	507							*b*
		542 w	527 w					*b*
				570 w	555	580	565	*b*
					575			
588	588	595 s	595	594 m	594	598	597	ν_{MeAs}
600 s, sh	601					600 m	600 m	
606 sh	607							
		615	614	614 sh	615 sh			ν_{MeAs}
622 s	622	624 vs	623	625 vs	625	622 vs	622 vs	ν_{ClO_4}
705	705	702 w	702 w	702	702	701	702	ν_{28} or ν_{14}
	712 w			713	714			
763		762 db	762 db	763 db	764 sh	755		ν_{18}
771	770 (ts)	769 m	770 m	771	772	768		
825 w, sh	825	820 sh		823 sh	821 sh			
834 w, sh	834	840 sh	840 sh	840 sh				Me rock
868 s	ts	866 s	866 s	864 s	866 s	865 s		Me rock
883 s	883 s			882 sh	884 sh	880 sh		Me rock
				904 sh	904 sh			
920 s	920 s	911 m	911 m	911 s	911 s	910 s		ν_{ClO_4}
960 m	960 m					958 w		
				1000 w				
				1007 w				
1032	1032	1029	1029 w	1030 m	1030 m	1030 sh		ν_8
1100 br, s	1100 br, s	1100 br, s	1100 br, s	1100 br, s	1100 br, s	1100 vs		ν_{ClO_4}
		1170	1170	1168 w	1168 w			ν_6
		1249	1248	1249	1250			ν_{26}
1259	1257	1262	1262	1262	1262	1264		
1266 w	1266 w	1268 w	1268 w	1268 w	1269 w			Me def
1283	1283	1280	1280	1279	1280	1282		ν_5
		1410 sh	1410 sh					
1423	1424	1422	1422 m	1422	1424 m	1422 m		ν_{24} and ν_4
1454	1453	1451 m	1450 m	1449 m	1449 m			
			1531					
1563	1563	1559	1558	1561 m	1561 m	1564 m	1564 m	ν_{23}
		1570		1569 w, sh				
1584 vw, br		1581		1598				
		1602	1575					*b*
				1633 vs	1604 vs	1634 s	1604	*b*
				1664	1632			*b*
1852 vs	1815 vs							*b*
						2064 s		ν_{NCS}
2932	2930	2922	2922	2922				C-H str
				2940				
				2965				
		2940	2940					
3015	3015	3015	3015					
		3040	3042					
		3070	3070	3067	3070			
		3135	3135					

[a] sh = shoulder, w = weak, m = medium, s = strong, v = very, br = broad, ts = too strong to measure accurately, db = doublet. [b] MNO skeletal vibrations; see text for discussion and Table IV for assignments.

species, the isotopic shifts provided assignments for ν_{NO}, ν_{FeN}, and δ_{FeNO} of each.

$[Co(NO)(en)_2(ClO_4)][ClO_4]$. The IR spectra of numerous ethylenediamine complexes have been reported.[27] Even though the IR spectra of ethylenediamine complexes have a large number of bands with variable intensities and positions, three bands at 1665, 568, and 494 cm^{-1} associated with the skeletal vibrations of the CoNO group were readily identified from their ^{15}N shifts. The results reported here for freshly prepared samples are in qualitative agreement with the brief report of Miki et al. However, because of the unusually large discrepancies between Miki's data[26] and our own (8 cm^{-1}), the IR spectrum of the sample used for the structure determination[28] was also obtained and found to be identical with that of our freshly prepared sample. Since each of the three bands reported by Miki for $[Co(NO)(en)_2(ClO_4)][ClO_4]$

Table III. Force Constants and Structural Parameters for the {MNO}^{n} Groups

compd	M-N, Å	M-N-O, deg	k_{MN}, mdyn/Å	k_{NO}, mdyn/Å	k_δ, mdyn Å	k_{int}	ref
$[Ru(NO)(DAS)_2Cl]Cl_2$[a]	1.75	180	5.5	13.8	0.99		1
$Fe(NO)(DMDTC)_2I$	1.66	175	4.8/n.c.[e]	13.2/12.9	0.9/0.8		16
$Fe(NO)(DMDTC)_2$	1.71	173	4.0	11.3	0.032/0.006[d]		21
$[Co(NO)(en)_2(ClO_4)][ClO_4]$	1.80	138	3.1	11.5	1.22	−0.75	28
$[Fe(NO)(DAS)_2Br][ClO_4]$[b]	1.70	148	2.7	11.5	0.94	−0.35	*b*
$[Co(NO)(DAS)_2Br][ClO_4]$[c]	1.87	132	2.1	10.9	0.86	−0.28	*c*
$[Co(NO)(DAS)_2][ClO_4]_2$	1.68	178	3.0	14.2	0.75, 0.66		14

[a] The average NO distance used for these calculations was 1.13 Å. See ref 1 for details. [b] R. W. Perry, Ph.D. Dissertation, University of Wisconsin, 1968. [c] The distances and angles were assumed to be the same as those for the thiocyanate derivative reported in ref 14. [d] Calculated using an FeNO angle of 180°. [e] Not calculated.

Table IV. Observed and Calculated Frequencies for the {MNO}^{n} Complexes Using the Three-Body Model[a]

	ν_{NO}				ν_{MN}				ν_{MNO}			
	^{14}N		^{15}N		^{14}N		^{15}N		^{14}N		^{15}N	
compd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd
$[Ru(NO)(DAS)_2Cl]Cl_2$	1882	1883	1844	1843	596	596	592	591	591	591	577	576
$Fe(NO)(DMDTC)_2I$	1830	1829	1794	1792	621	621	617	615	565	565	551	552
	1812	1812	1772	1773	550		546		542	542	530	530
$Fe(NO)(DMDTC)_2$	1692	1692	1655	1656	563	563	559	559	106	106	102	103
									46	46	43	44
$[Co(NO)(en)_2(ClO_4)][ClO_4]$	1665	1664	1631	1631	494	494	490	491	568	570	556	555
$[Fe(NO)(DAS)_2Br][ClO_4]$	1664	1665	1632	1632	455	455	452	452	570	569	555	555
	1633		1604									
$[Fe(NO)(DAS)_2(NCS)][ClO_4]$	1634	1635	1604	1602	463	463	458	459	580	579	565	565
$[Co(NO)(DAS)_2Br][ClO_4]$	1602	1603	1575	1573	371	370	368	368	542	542	527	527
$[Co(NO)(DAS)_2][ClO_4]_2$	1852	1852	1815	1815	491	491	486	486	506	506	494	494
									476	477	465	465

[a] The structural parameters and force constants used for these calculations are listed in Table II.

are at higher frequencies than the present data, these discrepancies are attributed to calibration errors. No bands below 200 cm^{-1} were found to shift with ^{15}N substitution, and the magnitude of the shifts observed for the bands at higher frequencies led to the assignments reported in Table IV.

DAS Complexes. There have been several extensive studies of the IR spectra of DAS complexes.[1,29,30] This ligand possesses a large number of rather strong IR bands, but only those in the 400–650-cm^{-1} region present any difficulties in identifying the skeletal vibrations of the MNO groups.[1]

trans-$[Fe(NO)(DAS)_2(NCS)][ClO_4]$ was chosen for these studies because convenient routes for its synthesis have been worked out[17] and an X-ray structural investigation of this compound is complete.[15] Three bands were found to shift with ^{15}NO substitution: ν_{NO}, 1634 → 1604 cm^{-1}, ν_{FeN}, 463 → 458 cm^{-1}, and δ_{FeNO}, 580 → 565 cm^{-1} (Table II). These bands all occur in regions of the spectrum which are relatively free from interference by DAS bands. No other bands were observed to shift with ^{15}N substitution, and the remaining bands in the IR spectrum could be associated with the known frequencies of the other ligands (DAS and NCS$^-$). The position of the NCS$^-$ band at 471 cm^{-1} is indicative of bonding of the thiocyanate ligand through the nitrogen atom[31] in agreement with the results of the single-crystal X-ray study.[15] The IR spectra of the closely related complex *trans*-$[Fe(NO)(DAS)_2Br][ClO_4]$ were also obtained. A total of four bands were observed to shift with ^{15}N substitution: ν_{NO}, 1664 → 1632 cm^{-1} and 1633 → 1604 cm^{-1}, ν_{FeN}, 455 → 452 cm^{-1}, and δ_{FeNO}, 570 → 555 cm^{-1}. The presence of two bands in the 1600-cm^{-1} region is not unusual for these nitrosyl complexes and is due to solid-state effects. The frequencies for ν_{FeN} are less reliably known because this weak band occurs as a shoulder on the strong 440-cm^{-1} band of DAS. The bending vibration, δ_{FeNO}, is considerably weaker than the corresponding bending vibrations of the linear RuNO group.[1]

The DAS derivative of {CoNO}^{8}, *trans*-$[Co(NO)(DAS)_2Br][ClO_4]$, was prepared with both ^{15}NO and ^{14}NO.

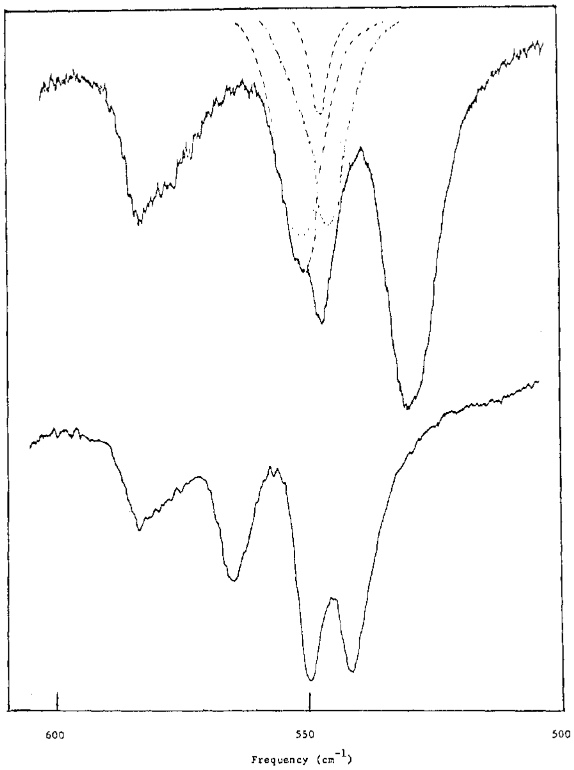

Figure 1. The infrared spectra of *cis*-$[Fe(^{14}NO)(DMDTC)_2I]$ (lower curve) and *cis*-$[Fe(^{15}NO)(DMDTC)_2I]$ (upper curve).

A total of three bands shifted on ^{15}NO substitution. The strongest band in the 1500–1700-cm^{-1} region was identified as ν_{NO} (1602 → 1575 cm^{-1}). The two bands below 600 cm^{-1} were assigned to ν_{CoN} and δ_{CoNO} on the basis of their observed isotopic shifts, 371 → 368 cm^{-1} and 542 → 527 cm^{-1}, respectively. The bending vibration, δ_{CoNO}, was considerably weaker than the corresponding bending vibration of $[Co(NO)(DAS)_2][ClO_4]_2$.

Substitution of ^{15}NO for ^{14}NO in $[Co(NO)(DAS)_2][ClO_4]_2$ produced shifts for four bands: ν_{NO}, 1852 → 1815 cm^{-1}, ν_{CoN}, 491 → 486 cm^{-1}, and the degenerate bending vibration, δ_{CoNO}, 506 → 494 cm^{-1} and 476 → 465 cm^{-1}. Splitting of the degenerate bending vibration has also been found for $[RuNO(DAS)_2Cl]^{2+}$. These bands assigned to bending vibrations have intensity comparable to that found for other DAS derivatives of linear MNO groups.

B. Calculations. The frequencies reported as "calculated" in Table IV were obtained from a general valence force field using the NORCRD program.[19] NORCRD was tested by duplicating the calculations of Herzberg[20] for H_2O, CO_2, and CS_2 and of Burns and Bernstein,[32] Landau and Fletcher,[33] and Eberhardt[34] for NOCl and NOBr. The agreement was deemed to be satisfactory.[35] The values of the force constants for the metal nitrosyls were systematically varied until agreement between the calculated and observed frequencies was equal to or less than the estimated experimental error (Table IV). The experimentally determined values for the bond distances and angles of the MNO complexes were utilized in these calculations. It was found that the quality of agreement which could be obtained between calculated and observed frequencies was very insensitive to the particular set of values used for the bond distances and bond angles.

For most of the complexes in this study, the calculations agreed with and confirmed observed ^{15}N frequency shifts. However, the bands at 285 and 43 cm^{-1} in $Fe(NO)(DMDTC)_2$ which appeared to shift by 3 cm^{-1} could not be fit to any combination of band assignments and were eliminated from consideration as possible fundamental vibrations of FeNO partially on this basis. Similarly, the two sets of bands for $Fe(NO)I(DMDTC)_2$ were assigned to two different forms partially on the basis of self-consistent calculations of the IR frequencies using NORCRD. Although it is probably possible to fit the present data set using more than three force constants for the linear MNO groups, there was no experimental justification for such a procedure, especially since in our hands, better agreement was obtained using only three force constants than was reported in the literature for a more complex eight-body model.[7] For the complexes with bent MNO groups, $[Co(NO)(en)_2(ClO_4)][ClO_4]$, $[Co(NO)(DAS)_2Br][ClO_4]$, $[Fe(NO)(DAS)_2Br][ClO_4]$, and $[Fe(NO)(DAS)_2(NCS)][ClO_4]$, it was necessary to introduce an interaction force constant to obtain satisfactory agreement between the observed frequencies and those calculated using the three-body model.

Discussion

The results of these spectral measurements are summarized in Tables I and II. The band assignments for the vibrations of the $\{MNO\}^n$ groups are summarized in Table IV. These assignments were based mainly on the observed isotopic shifts (ca. 30 cm^{-1} for ν_{NO}, 1–6 cm^{-1} for ν_{MN}, and 6–15 cm^{-1} for δ_{MNO}) as well as the spectral region in which they were found. In those few cases where some ambiguity existed, the bands were then assigned on the basis of their relative intensities (ν_{NO}, very strong, δ_{MNO}, medium to weak, and ν_{MN}, weak to very weak). These considerations resulted in all of the assignments listed in Table IV with one exception. As discussed above, the band found at 285 cm^{-1} in $Fe(NO)(DMDTC)_2$ appeared to undergo a 3-cm^{-1} shift with ^{15}N substitution, but its possible assignment as ν_{FeN} was eliminated by comparison with frequencies calculated using the triatomic model. The band at 563 cm^{-1} has an observed shift of 4 cm^{-1} and was assigned to ν_{FeN}. The frequencies of 106 and 46 cm^{-1} assigned to δ_{FeNO} are exceptionally low for metal nitrosyls. Structural studies[21] at room temperature indicated that the FeNO group in this complex is bent (160°), but the thermal parameters were abnormally large suggesting a disorder of the FeNO group or simply a large thermal motion of a "floppy" NO ligand. Redetermination of the structure at −80 °C reduced the thermal motion, but the FeNO group was more nearly linear (170.4°). These structural data indicate that the $\{FeNO\}^7$ group in this complex has a low barrier between linear and bent geometries consistent with the present IR studies and with the electronic structure which has been extensively discussed elsewhere.[11]

On the basis of these band assignments, the derived force constants were obtained (Table III) by matching the calculated frequencies species with the experimental results for both ^{15}N and ^{14}N species. The results of these calculations are summarized in Table IV. The maximum difference between observed and calculated frequencies is 2 cm^{-1} (two examples) while the averages deviated by only −0.18 cm^{-1} and the standard deviation was 0.54 cm^{-1}. Since this agreement between calculated and observed frequencies is well within the errors of the experiments, the agreement was considered satisfactory.

Conclusions

The initial paper in this series[1] demonstrated that the simple three-body model utilizing only diagonal force constants was sufficient to account for the vibrational frequencies of linear $\{RuNO\}^6$ and $\{RuN_2\}^6$ complexes. Miki reached similar conclusions for K_2RuCl_5NO by comparing the results of an eight-body calculation and the three-body calculations with the experimentally observed frequencies. When these studies were initiated, it had been hoped that the determination of a sufficient number of frequencies for isotopically substituted species would allow the MNO angle to be determined by fitting the data to the three-body model. Unfortunately, this proved to be impossible because the MNO frequencies are required to be known to better than ±1 cm^{-1} for this purpose. However, several questions regarding the three-body model remained unanswered. Is the three-body model limited (1) to linear or nearly linear MXY complexes, (2) to complexes which have interligand bond angles near 90°, (3) to the complexes of heavy metals (second- or third-row metals), and (4) to complexes in which the other ligands attached to the metal are dissimilar to the MXY group?

The results of this study clearly show that the three-body model will reproduce the frequencies of first-, second-, and third-row transition-metal nitrosyls. Moreover, the quality of agreement between calculated and observed frequencies is not dependent upon the interligand bond angles which range from 70 to 100°. Most importantly, it has been found that the three-body model applies equally well to linear and nonlinear MNO complexes *provided* an interaction constant is introduced for the nonlinear MNO complexes. Finally, an examination of the results in the literature suggests that the three-body approximation will not apply to complexes with two or more NO groups attached to the metal.

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Registry No. $[Ru(NO)(DAS)_2Cl]Cl_2$, 31237-88-4; $Fe(NO)(DMDTC)_2I$, 62637-83-6; $Fe(NO)(DMDTC)_2$, 14263-11-7; $[Co(NO)(en)_2(ClO_4)][ClO_4]$, 60384-76-1; $[Fe(NO)(DAS)_2Br][ClO_4]$, 16999-65-8; $[Fe(NO)(DAS)_2(NCS)][ClO_4]$, 63102-37-4; $[Co(NO)(DAS)_2Br][ClO_4]$, 66777-80-8; $[Co(NO)(DAS)_2][ClO_4]_2$, 53495-87-7; $Co(NO)(DMDTC)_2$, 36434-42-1; *cis*-$[Fe(^{14}NO)(DMDTC)_2I]$, 62637-83-6; *cis*-$[Fe(^{15}NO)(DMDTC)_2I]$, 66777-78-4.

References and Notes

(1) M. S. Quinby and R. D. Feltham, *Inorg. Chem.*, **11**, 2468 (1972).
(2) B. F. G. Johnson and J. A. McCleverty, *Prog. Inorg. Chem.*, **7**, 277 (1966).
(3) J. Lewis, R. J. Irving, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **7**, 32 (1958).
(4) R. D. Feltham and R. S. Nyholm, *Inorg. Chem.*, **4**, 1334 (1965).
(5) A. P. Gaughan, B. L. Haymore, J. A. Ibers, W. H. Myers, T. F. Nappier, and D. W. Meek, *J. Am. Chem. Soc.*, **95**, 6859 (1973).
(6) B. L. Haymore and J. A. Ibers, *Inorg. Chem.*, **14**, 3069 (1975).
(7) E. Miki, *Bull. Chem. Soc. Jpn.*, **41**, 1835 (1968).
(8) E. Miki, S. Kubo, K. Mizumachi, T. Ishimori, and H. Okuno, *Bull. Chem. Soc. Jpn.*, **44**, 1024 (1971).
(9) M. J. Cleare, H. P. Fritz, and W. P. Griffith, *Spectrochim. Acta, Part A*, **28a**, 2031 (1972).
(10) C. G. Pierpont and R. Eisenberg, *J. Am. Chem. Soc.*, **93**, 4905 (1971).
(11) J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, **13**, 339 (1974).
(12) R. Eisenberg and C. D. Mayer, *Acc. Chem. Res.*, **8**, 26 (1975).
(13) J. H. Enemark and R. D. Feltham, *J. Chem. Soc.*, 718 (1972).
(14) J. H. Enemark, R. D. Feltham, J. Riker-Nappier, and K. F. Bizot, *Inorg. Chem.*, **14**, 624 (1975).
(15) J. H. Enemark, R. D. Feltham, B. T. Huie, P. L. Johnson, and K. Bizot Swedo, *J. Am. Chem. Soc.*, **99**, 3285 (1977).
(16) O. A. Ileperuma and R. D. Feltham, *Inorg. Chem.*, **16**, 1876 (1977).
(17) T. E. Nappier, R. D. Feltham, J. H. Enemark, A. Kruse, and M. Cooke, *Inorg. Chem.*, **14**, 806 (1975).
(18) W. M. Poteet and R. D. Feltham, *Appl. Spectrosc.*, **27**, 135 (1972).
(19) Program No. 177, NORCRD, written by Dr. W. Gwinn, was obtained from the Quantum Chemistry Program Exchange, Indiana University, and some minor modifications were made to adapt it to local use.
(20) G. Herzberg, "Infrared and Raman Spectra", Van Nostrand-Reinhold, New York, N.Y., 1948.
(21) M. Colapietro, A. Domenicano, L. Scaramuzza, A. Vaciago, and L. Zambonelli, *Chem. Commun.*, 583 (1967); G. R. Davies, R. H. B. Mais, and P. G. Owston, *ibid.*, 81 (1968); G. R. Davies, J. A. J. Jarvis, B. K. Kilbourn, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc.*, 1275 (1970).
(22) S. H. Simonsen and M. H. Mueller, *J. Inorg. Nucl. Chem.*, **27**, 309 (1965).
(23) For example, see: D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc. A*, 1152 (1969); A. H. Ewald, R. L. Martin, I. G. Ross, and A. H. White, *Proc. R. Soc. London, Ser. A*, **280**, 235 (1964).
(24) K. A. Jensen, B. M. Dahl, P. H. Nielsen, and G. Borch, *Acta Chem. Scand.*, **24**, 2029 (1971).
(25) K. A. Jensen, B. M. Dahl, P. H. Nielsen, and G. Borch, *Acta Chem. Scand.*, **26**, 2241 (1972).
(26) E. Miki, K. Mizumachi, T. Ishiomori, and H. Okuno, *Bull. Chem. Soc. Jpn.*, **46**, 3779 (1973).
(27) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley, New York, N.Y., 1973.
(28) P. L. Johnson, J. H. Enemark, R. D. Feltham, and K. Bizot Swedo, *Inorg. Chem.*, **15**, 2989 (1976).
(29) J. H. S. Green, W. Kynaston, and G. A. Rodley, *Spectrochim. Acta, Part A*, **24a**, 863 (1968).
(30) G. B. Deacon and J. H. S. Green, *Spectrochim. Acta, Part A*, **24a**, 959 (1968).
(31) D. M. Adams, "Metal-Ligand and Related Vibrations", St. Martin's Press, New York, N.Y., 1968, pp 318–319.
(32) W. G. Burns and H. G. Bernstein, *J. Chem. Phys.*, **18**, 1669 (1950).
(33) L. Landau and W. H. Fletcher, *J. Mol. Spectrosc.*, **4**, 276 (1960).
(34) W. H. Eberhardt and T. G. Burke, *J. Chem. Phys.*, **20**, 529 (1952).
(35) M. S. Quinby-Hunt and R. D. Feltham, to be submitted for publication.

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Nuclear Magnetic Resonance Study of Metal Complexes. 2. Conformations of 1,2-Diamine Chelate Rings with *C*-Phenyl Group(s) in Cobalt(III) and Platinum(II) Complexes

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The proton magnetic resonance spectra of $[Co(CN)_4(R\text{-phenen})]^-$ (*R*-phenen = (*R*)-phenylethylenediamine), $[Pt(NH_3)_2(pn\text{-}d_1)]^{2+}$ (pn-d_1, = 2-deuterio-1,2-diaminopropane), $[Pt\ (S\text{-pn-}d_2)_2]^{2+}$ (S-pn-d_2 = (2*S*)-1,1-dideuterio-1,2-diaminopropane), $[Pt(S,S\text{-bn})_2]^{2+}$ (*S,S*-bn = (2*S*,3*S*)-2,3-butanediamine), and $[Pt\ (en)((-)_D\text{-stien})]^{2+}$ ($(-)_D$-stien = stilbenediamine) have been measured. The ^{13}C NMR spectra of these Pt(II) complexes and $[Pt(en)(R\text{-phenen})]^{2+}$ have been obtained. Values of $J_{H-C-C-H}$ indicate a strong preference for the equatorial orientation of $C-C_6H_5$ in (*R*)-phenylethylenediamine of Co(III) complexes. For Pt(II) complexes, values of $J_{Pt-N-C-H}$ and $J_{Pt-N-C-C}$ suggest that 1,2-diaminopropane (propylenediamine) and (*R*)-phenylethylenediamine chelate rings have unsymmetrical gauche conformations and (2*S*,3*S*)-2,3-butanediamine and $(-)_D$-stilbenediamine chelate rings take symmetrical gauche conformations, while *meso*-stilbenediamine chelate changes its conformation rapidly from λ to δ and vice versa rapidly on the NMR time scale. For the diamine chelates with *C*-phenyl group(s) a Karplus-like dihedral angle dependence for the $J_{Pt-N-C-C^*}$, where C* is a phenyl carbon atom which attaches on the membered-carbon atom, was observed. These $^3J_{Pt-C^*}$ values were very similar to those for the $J_{Pt-N-C-CH_3}$ in the diamine chelates with *C*-methyl group(s).

Introduction

Methyl groups substituted to diamines or tetraamines are capable of affecting the configurations of metal complexes. Little information has, however, been obtained for other substituted groups. In our recent research,[1] abnormal circular dichroism (CD) curves were observed for *trans*-$[CoCl_2(R\text{-phenen})_2]^+$ and *trans*-$[CoCl_2((-)_D\text{-stien})_2]^+$, where *R*-phenen and $(-)_D$-stein are (*R*)-phenylethylenediamine and $(-)_D$-stilbenediamine, respectively. It is accepted that the puckered dissymmetric conformation of ligand in the *trans*-$[CoCl_2$(optically active 1,2-diamine)$_2]^+$ ions contributes predominantly to the CD curve.

It is very interesting to clarify the stereochemical behavior of a phenyl group substituted to 1,2-diamines such as phenen and stien.

Our earlier NMR study of Co(III), Pd(II), and Pt(II) complexes of (*R*)-propylenediamine (*R*-pn) established the ligand conformation in aqueous solution on the basis of the J_{H-H} value of the ligand H–C–C–H fragments.[2]

Since the methylene and methine parts of the *R*-phenen chelate ring have an ABC spin system which is formally equivalent to those of the propylenediamine chelate ring, the conformational analysis method which has been useful in analyzing the propylenediamine chelate ring would be applicable to this diamine.

On the other hand, $(-)_D$-stein has two chemically equivalent methine protons, and the $J_{H-C-C-H}$ value could not be observed. Therefore, it is impossible to employ the conformational analysis based on the J_{H-H} value to this ligand. Some recent research[3,4] suggests that the dihedral angle dependence of the J_{Pt-H} value for Pt–N–C–H fragments in Pt(II) complexes of amino acid or 1,3-diamine seems to parallel that of the J_{H-H} for H–C–C–H fragments. We suppose it will be possible to achieve the conformational analysis of the stien chelate ring by employing the $J_{Pt-N-C-H}$ value.

It is well-known that amino acidato chelate rings are nearly planar compared with 1,2-diamine chelate rings and the angle at the metal for the 1,3-diamine chelate ring is larger than

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