observed for any of the other complexes.

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(18) The ultraviolet spectra of $Co(H_2Me_2L)^{3+}$ and $Co(Me_2L)^+$ are reported[6] to be somewhat different. This is not substantiated by the present work. $Co(H_2Me_2L)^{3+}$ and $Co(Me_2L)^+$ have practically identical spectra in the range 25,000–46,000 cm^{-1}.

(19) The *Dq* values of $Ni(NH_3)_6{}^{2+}$ and $Co(NH_3)_6{}^{3+}$ are 1080 and 2490 cm^{-1}, respectively.[20,21] Assuming that the *Dq* is amplified in the same ratio in going from $Ni(H_2Me_2L)^{2+}$ to $Co(H_2Me_2L)^{3+}$, the calculated value of ν_1 for the latter complex is ~26,000 cm^{-1}. In this calculation $(Dq)_{Ni}$ (i.e., *Dq* of $Ni(H_2Me_2L)^{2+}$) is taken as 1300 cm^{-1} so that $(Dq)_{Co}$ is ~3000 cm^{-1}; ν_1 is obtained from the relationship $\nu_1 = 10(Dq)_{Co} - C$, where[21] *C*, the interelectronic repulsion parameter, is ~4000 cm^{-1}.

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Skeletal Vibrational Spectra, Force Constants, and Bond Properties of Transition Metal Ammine Complexes

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A systematic investigation of skeletal ir and Raman data, force constants, and bond properties has been carried out for all octahedral hexaammine and tetrahedral and square-planar tetraammine complexes of the transition metals (including zinc and cadmium) for which reliable vibrational frequencies are known. The calculations are based on critically selected spectral data reported in the literature and on vibrational frequencies measured by ourselves. A correlation of the metal–nitrogen stretching force constants to other physical properties as well as to symmetry of the complexes, oxidation numbers, and position of the central atoms in the periodic system yields reasonable results.

Introduction

Although transition metal ammine complexes are among the best known complex compounds and although a great deal of vibrational spectroscopic work has been done in this field during the last two decades, reliable Raman data for most of the complexes of divalent metals have not yet been reported. Previous normal coordinate analyses for ammine complexes have been based mainly upon infrared vibrational frequencies using the Urey–Bradley potential function. For many complexes a comparison of the force constants reported in the literature reveals large discrepancies. In some cases the metal–nitrogen stretching force constants, which are very useful for understanding the nature of bonding in complexes, differ by more than 100%.[1]

It is the aim of this paper to report trustworthy skeletal force constants of ammine complexes determined from reliable infrared and Raman frequencies and by use of appropriate models. We will inspect whether the metal–nitrogen stretching force constants calculated by us can be correlated with other physical data and whether a comparison of the bond properties of the complexes with regard to symmetry, oxidation number, and position of the central atom in the periodic system yields reasonable results. The calculations for all octahedral hexaammine and tetrahedral and square-planar tetraammine complexes of the transition metals (including zinc and cadmium), for which skeletal vibrational frequencies are known, will be made on the basis of critically selected literature data and of frequencies measured by ourselves. Some skeletal vibrational frequencies (particularly Raman data) will be presented here for the first time.

Experimental Section

$[Cr(NH_3)_6]Cl_3$, $[Co(NH_3)_6]Cl_2$, $[Ni(NH_3)_6]Cl_2$, $[Cu(NH_3)_4]SO_4{\cdot}H_2O$, and $[Pd(NH_3)_4]Cl_2{\cdot}H_2O$ were prepared by standard methods[2–4] and $[Mn(NH_3)_6]Cl_2$ and $[Fe(NH_3)_6]Cl_2$ by introducing gaseous ammonia into aqueous solutions of NH_4Cl, $MnCl_2{\cdot}4H_2O$, and $FeCl_2{\cdot}4H_2O$, respectively (cf. ref 5). $[Cd(NH_3)_4](ReO_4)_2$ was prepared according to ref 6 and 7. $[Mn(NH_3)_6]^{2+}$, $[Co(NH_3)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$, and $[Cd(NH_3)_6]^{2+}$ in aqueous solutions have been obtained by adding concentrated aqueous ammonia to solutions of the corresponding chlorides. In the case of the manganese and cobalt complexes, small quantities of hydrazine were necessary to stabilize the divalent state of the metals.

Infrared spectra of Nujol mulls were measured on a Perkin-Elmer IR-180 spectrometer. Raman spectra of the aqueous solutions mentioned above and of $[Cd(NH_3)_4](ReO_4)_2$ were scanned with a Coderg laser Raman spectrometer PHO using a Kr^+ laser from Spectra-Physics (excitation lines 6471 and 4762 Å). Raman lines due to intermediate steps of complex formation in aqueous solution were not observed. The laser Raman spectra of the solid hexaammine-manganese, -iron, -cobalt, -nickel, and -cadmium complexes could not be measured (not even with the rotating cell technique) because of sample decomposition. Even in the presence of reducing agents, the central atom in solutions containing $[Fe(NH_3)_6]^{2+}$ was oxidized to the trivalent state ($Fe(OH)_3$ precipitate) in the course of the Raman measurement. The spectrometers were calibrated with water vapor and krypton plasma lines, respectively.

Vibrational Spectra

Hexaammine Complexes of Divalent Metals. No skeletal Raman frequencies for octahedral hexaammine complexes of divalent transition metals in aqueous solution other than the totally symmetric metal–nitrogen stretching vibrations of $[Ni(NH_3)_6]^{2+}$ and $[Cd(NH_3)_6]^{2+}$ have been previously reported.[8,9] In a recent publication,[1] we could confirm the position of $\nu_s(NiN)$ in the Raman spectrum of $[Ni(NH_3)_6]^{2+}$. Furthermore, a new line at 235 cm^{-1} appearing as a shoulder in the slope of the laser exciting line was observed and assigned to $\delta(NNiN)(F_{2g})$. Damaschun[9] erroneously assigned a line of $[Zn(NH_3)_4]^{2+}$ to the corresponding hexaammine complex, which does not exist in aqueous solution.

The Raman solution data determined by us are presented in Table I. Unfortunately, only one line (instead of three lines expected) in the region of the skeletal vibrations could be observed for $[Mn(NH_3)_6]^{2+}$ and $[Cd(NH_3)_6]^{2+}$ (unequivocally assigned to the totally symmetric stretching vibration $\nu_s(MN)(A_{1g})$ from depolarization measurements). A careful investigation of the Raman spectra of $[Co(NH_3)_6]^{2+}$ and $[Ni(NH_3)_6]^{2+}$ revealed (in addition to the lines corresponding

Table I. Skeletal Vibrational Frequencies[a] of Octahedral Hexaammine Complexes (cm^{-1})

	$\nu_1(A_{1g}) = \nu_s(MN)$ Raman	$\nu_2(E_g) = \nu(MN)$ Raman	$\nu_3(F_{1u}) = \nu_{as}(MN)$ Ir	$\nu_4(F_{1u}) = \delta_{as}(NMN)$ Ir	$\nu_5(F_{2g}) = \delta(NMN)$ Raman	$\nu_6(F_{2u}) = \delta(NMN)$
$[Mn(NH_3)_6]^{2+}$	330	(235)[b]	302	165		
$[Fe(NH_3)_6]^{2+}$	344[c]	(245)[b]	315	170		
$[Co(NH_3)_6]^{2+}$	357	~255	325	192		
$[Ni(NH_3)_6]^{2+}$	370	~265	334.5	215	235	
$[Zn(NH_3)_6]^{2+}$	(340)[b]	(235)[b]	300	(165)[b]		
$[Cd(NH_3)_6]^{2+}$	342	(235)[b]	298	(165)[b]		
$[Cr(NH_3)_6]^{3+}$	465	412	468.5	268	270	206
$[Co(NH_3)_6]^{3+}$	494	442	474.7	331	322	
$[Ru(NH_3)_6]^{3+}$	500	475	463	273	248	
$[Rh(NH_3)_6]^{3+}$	514	483	472	294.5	240	
$[Os(NH_3)_6]^{3+}$	(515)[b]	(490)[b]	452	256		
$[Ir(NH_3)_6]^{3+}$	527	500	475	272	262	
$[Pt(NH_3)_6]^{4+}$	569	545	530	318	288	

[a] For further details see text. [b] Estimated value. [c] Interpolated value.

to $\nu_s(CoN)(A_{1g})$, $\nu_s(NiN)(A_{1g})$, and $\delta(NNiN)(F_{2g})$) a very weak line in each case at about 255 and 265 cm^{-1}, respectively, which may be assigned to $\nu(MN)(E_g)$. Though the Raman spectrum of $[Fe(NH_3)_6]^{2+}$ could not be obtained (see Experimental Section), the value for $\nu_s(FeN)$ could be determined quite accurately by graphical interpolation. Our determination of the fully polarized Raman line of $[Cd(NH_3)_6]^{2+}$ confirmed previous work.[9] All E_u data in Table I in parentheses can only be taken as rough estimates with much uncertainty.

Reliable solid state Raman spectra for hexaammine complexes of divalent metal ions are not yet known. The frequencies for hexaamminecobalt and -nickel (with various anions) reported recently by Grzybek et al.[10] seem to be incorrect. In the case of the cobalt(II) complex, their skeletal data correspond approximately to those for hexaamminecobalt(III).

Our solid state infrared data for $[Co(NH_3)_6]Cl_2$ and $[Ni(NH_3)_6]Cl_2$ given in Table I agree well with previously reported skeletal vibrational frequencies (cf. ref 10 and 11). Despite the existence of many well established ir data for these complexes, ir spectroscopic information for the other hexaammines with divalent central atoms is very poor. To our knowledge, Sacconi, Sabatini, and Gans[11] were the only ones to report the ir spectra of $[Mn(NH_3)_6]Cl_2$ and $[Fe(NH_3)_6]Cl_2$, but they did not determine the antisymmetric skeletal deformation vibration. Their $\nu_{as}(MN)$ data turned out to be a little higher than the frequencies measured by us. Our stretching and deformation mode data can be taken from Table I. Two different frequencies for $\nu_{as}(MN)(F_{1u})$ of $[Zn(NH_3)_6]Cl_2$ and $[Cd(NH_3)_6]Cl_2$, respectively, have been reported in the literature.[8,11] The frequencies determined by Terrasse, Poulet, and Mathieu[8] seem to correspond to bands of the tetraammine complexes (cf. ref 11).

Although $[Ru(NH_3)_6]Cl_2$ is a well-known complex compound, reliable skeletal vibrational frequencies are not known. Whereas Fairey and Irving[12] observed a weak ir band at 437 cm^{-1} which they assigned to $\nu_{as}(RuN)$, Allen and Senoff[13] were not able to detect any band in this region. We expect the ir active stretching vibration for hexaammines with divalent central atoms to be at much lower wave numbers than 437 cm^{-1}. For the same reason, the ir data for $[V(NH_3)_6]Cl_2$ reported by Behrens and Lutz[14] do not seem very reliable. Both complexes will not be considered further in this paper.

Hexaammine Complexes of Trivalent Metals, $[Pt(NH_3)_6]^{4+}$. Reliable Raman data for many hexaammines of trivalent metal ions have been known for many years. The Raman spectrum of $[Cr(NH_3)_6]^{3+}$ in aqueous solution (He–Ne excitation) is partly superimposed by a well-resolved resonance phosphorescence spectrum, and the position of the ir and Raman forbidden but vibronically allowed F_{2u} skeletal mode could be determined from the vibrational structure of the $^2E_g \leftrightarrow {}^4A_{2g}$ transition. The Raman solution data for hexaamminechromium given in Table I are those reported by Long and Penrose,[15] the data for hexaamminecobalt were taken from Swaddle, Craig, and Boorman,[16] and the data for $[Ru(NH_3)_6]^{3+}$, $[Rh(NH_3)_6]^{3+}$, and $[Ir(NH_3)_6]^{3+}$ were from Griffith.[17] Skeletal Raman frequencies for $[Os(NH_3)_6]^{3+}$ have not yet been reported. The A_{1g} and E_g stretching frequencies of Table I are estimated values which have been determined by comparison with the ruthenium, rhodium, and iridium data. $\nu_s(PtN)(A_{1g})$ and $\nu(PtN)(E_g)$ have been obtained from the solution spectrum[18] and $\delta(NPtN)(F_{2g})$ from the solid state Raman spectrum of the chloride.[19]

Table II. Skeletal Vibrational Frequencies of Tetrahedral Tetraammine Complexes (cm^{-1})

	$\nu_1(A_1) = \nu_s(MN)$ Raman	$\nu_2(E) = \delta_s(NMN)$ Raman	$\nu_3(F_2) = \nu_{as}(MN)$ Raman, ir	$\nu_4(F_2) = \delta_{as}(NMN)$ Raman, ir
$[Co(NH_3)_4]^{2+}$	~405	195	430	195
$[Zn(NH_3)_4]^{2+}$	431.2	156.5	411.5	156.5
$[Cd(NH_3)_4]^{2+}$	386	~170	369.5	163

Our solid state ir data for $[Cr(NH_3)_6](NO_3)_3$ given in Table I agree well with those reported by Siebert and Eysel,[20] but one shoulder at 460 cm^{-1} observed by them could not be corroberated. Recently we solved the continuing controversy over the assignment of the metal–nitrogen stretching vibrations in the infrared spectrum of $[Co(NH_3)_6]Cl_3$ by intensity considerations and by comparison of calculated and measured $^{14}N/^{15}N$ and H/D frequency shifts.[21] Table I contains the average value of the $\nu_{as}(CoN)(F_{1u})$ triplet determined by us. The ir frequencies for the other complexes (chlorides) given in the table are those determined by Griffith[17] and by Nolan and James;[19] for $[Ru(NH_3)_6]Cl_3$ and $[Rh(NH_3)_6]Cl_3$ we used the average values of the $\delta_{as}(NMN)(F_{1u})$ doublets reported in ref 17.

Tetraammine Complexes. Only few data are available for tetrahedral tetraammine complexes. Müller, Christophliemk, and Tossidis[22] reported the solid state infrared spectrum of $[Co(NH_3)_4](ReO_4)_2$. Their $\nu_{as}(CoN)(F_2)$ and $\delta_{as}(NCoN)(F_2)$ values are given in Table II, together with $\nu_{as}(CoN)(A_1)$, the only line which could be observed in the Raman spectrum (apart from lines pertaining to the anion). The Raman active mode $\delta_{as}(NCoN)(E)$ was assumed to be accidentally degenerated with the antisymmetric skeletal deformation mode. Ir and Raman spectra of $[Zn(NH_3)_4]I_2$ are well established. Our skeletal data reported recently[21] agree well with those determined by Nakamoto, Takemoto, and Chow.[23] Since the degeneracy of $\nu_{as}(ZnN)(F_2)$ is removed in the ir spectrum but not in the Raman spectrum,[21] only the solid state Raman frequencies are considered in Table II. In aqueous solution

Table III. Skeletal Vibrational Frequencies of Square-Planar Tetraammine Complexes (cm^{-1})

	$\nu_1(A_{1g}) = \nu_s(MN)$ Raman	$\nu_2(B_{1g}) = \nu(MN)$ Raman	$\nu_3(B_{2g}) = \delta(NMN)$ Raman	$\nu_4(A_{2u}) = \gamma(NMN)$ Ir	$\nu_5(B_{2u}) = \tau(NMN)$	$\nu_6(E_u) = \nu_{as}(MN)$ Ir	$\nu_7(E_u) = \delta_{as}(NMN)$ Ir
$[Cu(NH_3)_4]^{2+}$	420	375		226		425.5	256
$[Pd(NH_3)_4]^{2+}$	510	468	305	237		494	291
$[Pt(NH_3)_4]^{2+}$	538	526	270	235		510	297

Raman spectra, only $\nu_s(ZnN)(A_1)$ could be observed.[23,24]

The solid state Raman spectrum of $[Cd(NH_3)_4](ReO_4)_2$ is reported here for the first time. In addition to lines corresponding to the anion, we observed one intense line at 386 cm^{-1} and a very weak shoulder at about 170 cm^{-1} in the slope of the excitation line, which we assign to $\nu_s(CdN)(A_1)$ and $\delta_s(NCdN)(E)$ and/or $\delta_{as}(NCdN)(F_2)$, respectively. Plane[24] erroneously assigned the totally symmetric Cd–N stretching frequency of $[Cd(NH_3)_6]^{2+}$ in aqueous solution to $\nu_s(CdN)$ of tetraamminecadmium. Our solid state ir data of $[Cd(NH_3)_4](ReO_4)_2$ given in Table II (the value for $\delta_{as}(NCdN)(F_2)$ is the average of a doublet) confirm a previous report.[25] No reliable data for $[Hg(NH_3)_4]^{2+}$ are available. The frequencies reported in the literature (cf. ref 24 and 26) possibly pertain to the diammine complex.

The skeletal vibrational frequencies for square-planar tetraammine complexes are collected in Table III. The Raman solution data for $[Cu(NH_3)_4]^{2+}$ have recently been obtained by us,[27] the solid state Raman frequencies of $[Pd(NH_3)_4]Cl_2$ are those reported by Hendra,[28] and the solution data for $[Pt(NH_3)_4]^{2+}$ given in the table have been obtained by Mathieu.[29] The ir active in-plane and out-of-plane NMN deformation vibrations for square-planar ammine complexes have been assigned in the literature in a different manner. For $[Cu(NH_3)_4]^{2+}$, this problem has recently been solved by the comparison of measured and calculated H/D and $^{14}N/^{15}N$ shifts.[27,30] We have chosen the corresponding assignment for the palladium[27] and platinum complexes. Our solid state ir data for $[Cu(NH_3)_4]SO_4 \cdot H_2O$ and $[Pd(NH_3)_4]Cl_2 \cdot H_2O$ reported in Table III are comparable with those determined by Nakagawa and Shimanouchi[31] and Hiraishi, Nakagawa, and Shimanouchi,[32] respectively (the skeletal deformation vibrations are not assigned in ref 31). The ir frequencies of $[Pt(NH_3)_4]Cl_2$ obtained by the latter authors[32] are also included in the table.

Force Constants and Bond Lengths

The determination of force constants for octahedral hexaammine and tetrahedral and square-planar tetraammine complexes requires the solution of third-, fourth-, and seventh-order inverse eigenvalue problems. Even by using complete infrared and Raman data sets and all possible isotope shifts of the vibrational frequencies as additional data, the problem remains entirely underdetermined.[1] Urey–Bradley force constants calculated on the basis of seven ir active F_{1u}, F_2, and E_u vibrational frequencies, respectively, are not very trustworthy. On the one hand, additional constraints are necessary, which can be estimated only very arbitrarily, but which have much influence on the final force constants (see, e.g., ref 31). On the other hand, the Raman data are disregarded, and the calculations do not give reliable M–N stretching force constants if the Raman and ir active metal–nitrogen stretching frequencies differ by more than several wave numbers. As can be seen from the tables, this applies to many complexes.

Model calculations for a complete transition metal ammine complex reveal that the skeletal vibrations are only slightly coupled with the ligand vibrations; thus the ammonia ligands can be approximately regarded as dynamic units, by which the order of the secular equations is drastically reduced to $n = 1$ and 2. Recently we showed for a number of ammine complexes that reasonable skeletal force constants can be calculated from Raman and infrared data by using the point mass model and metal isotope as well as $^{14}N/^{15}N$ and H/D shifts of the vibrational frequencies as additional data.[1,21,27] The reliability of our so-called pseudo-exact force constants has been confirmed by calculations for the whole ions of $[Zn(NH_3)_4]^{2+}$ and $[Cu(NH_3)_4]^{2+}$ (ref 30 and 33) which are based on a force constant method developed by Cyvin[34] in which special symmetry coordinates for ligand vibrations, ligand-framework couplings, and framework vibrations are used.

For those complexes, for which reliable isotope shifts of the skeletal vibrational frequencies have not yet been determined, supplementary assumptions are necessary to determine the skeletal symmetry force constants of second-order secular equations. We have calculated these force constants for all ammine complexes given in Tables I to III by using the Urey–Bradley potential function,[35] the Fadini method,[36] and the **L** matrix approximation ($L_{ij}(j > i) = 0$).[37] A comparison of these data, the numerical values of which are not given here, with the force constants obtained by help of isotopic frequency shifts does not reveal satisfactory agreement in all cases. In general, the symmetry force constants calculated with the last-named approximation method turned out to be somewhat close to those determined by help of isotopic data, but we wish to emphasize that the determination of trustworthy skeletal symmetry force constants in second-order secular equations is only possible by using additional data. On the other hand, the inner GVFF metal–nitrogen stretching force constants $f(MN)$ calculated from the **L** matrix approximation data and the A_{1g}, E_g (O_h), A_1 (T_d), and A_{1g}, B_{1g} (D_{4h}) stretching frequencies, respectively, agree well with the pseudo-exact data within an error of 5%. One can assume with some certainty that the inaccuracies in the approximate $f(MN)$ values for those complexes, for which no pseudo-exact data are known, are of comparable order of magnitude.

Table IV presents the GVFF metal–nitrogen stretching force constants $f(MN)$ of 19 ammine complexes arranged in a periodic system in consideration of oxidation number of the central atom and symmetry of the complex. For the sake of conformity, the **L** matrix approximation values are reported throughout. In cases where one or two stretching frequencies had to be estimated (see Tables I–III), the second decimal of $f(MN)$ is written as a superscript. The metal–nitrogen bond orders which have been estimated according to the approximation given by Siebert[38] are also included in the table.

Accurate metal–nitrogen bond lengths determined by X-ray diffraction are known for only a few transition metal ammine complexes. Table V contains some recent data, together with the sums of estimated covalent and ionic radii.

Discussion

As can be seen from Table I, the metal–nitrogen stretching vibrations for hexaammine complexes of divalent transition metals occur in the range 230 to 370 cm^{-1}, for hexaammine complexes of trivalent metals between 400 and 530 cm^{-1}, and for $[Pt(NH_3)_6]^{4+}$ between 530 and 570 cm^{-1}. The totally symmetric M–N stretching vibrational frequency for each complex (except for $[Cr(NH_3)_6]^{3+}$) is higher than the other two stretching frequencies. It is interesting to note that $\nu(MN)(E_g)$ is lower than $\nu_{as}(MN)(F_{1u})$ in the case of the first

Table IV. GVFF Metal-Nitrogen Stretching Force Constants (mdyn/Å) and Bond Orders[a] of Transition Metal Ammine Complexes ($X = NH_3$)

	VIa	VIIa	VIII			Ib	IIb
O_h		MnX_6^{2+} 0.6_7 (0.3)	FeX_6^{2+} 0.7_3 (0.3)	CoX_6^{2+} 0.8_0 (0.3)	NiX_6^{2+} 0.85 (0.4)		ZnX_6^{2+} 0.6_9 (0.3)
	CrX_6^{3+} 1.66 (0.6)			CoX_6^{3+} 1.86 (0.6)			
T_d				CoX_4^{2+} 1.44 (0.5)			ZnX_4^{2+} 1.43 (0.5)
D_{4h}						CuX_4^{2+} 1.42 (0.5)	
O_h							CdX_6^{2+} 0.7_3 (0.4)
			RuX_6^{3+} 2.01 (0.8)	RhX_6^{3+} 2.10 (0.8)			
T_d							CdX_4^{2+} 1.24 (0.5)
D_{4h}					PdX_4^{2+} 2.15 (0.8)		
O_h			OsX_6^{3+} 2.1_3 (0.9)	IrX_6^{3+} 2.28 (0.9)			
					PtX_6^{4+} 2.75 (1.0)		
D_{4h}					PtX_4^{2+} 2.54 (1.0)		

[a] In parentheses.

Table V. Metal-Nitrogen Bond Lengths in Transition Metal Ammine Complexes and Sums of Covalent and Ionic Radii (Å)

	d(MN)	Sum of covalent radii	Sum of ionic radii
$[Cr(NH_3)_6]CuCl_5$	2.064[a]	1.93	2.40
$[Co(NH_3)_6]Cl_2$	2.114[b]	1.91	2.45
$[Co(NH_3)_6]I_3$	1.936[b]	1.91	2.34
$[Cu(NH_3)_4]SO_4 \cdot H_2O$	2.032[c]	1.92	2.40
$[Ru(NH_3)_6]Cl_2$	2.144[d]	2.00	
$[Ru(NH_3)_6](BF_4)_3$	2.104[d]	2.00	2.40
$[RhH(NH_3)_5](ClO_4)_2$	2.071[e]	2.00	2.40
$[Ir(SCN)(NH_3)_5](ClO_4)_2$	2.121[f]	2.02	
$[Pt(NH_3)_4]_2[Re_2O_3(CN)_8]$	2.051[g]	2.05	2.51

[a] K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, 7, 1111 (1968); S. A. Goldfield and K. N. Raymond, *ibid.*, 10, 2604 (1971). [b] N. E. Kime and J. A. Ibers, *Acta Crystallogr., Sect. B*, **25**, 168 (1969). [c] B. Morison, *ibid.*, **25**, 19 (1969). [d] H. C. Stynes and J. A. Ibers, *Inorg. Chem.*, **10**, 2304 (1971). [e] Average value of four equatorial bonds: B. A. Coyle and J. A. Ibers, *ibid.*, **11**, 1105 (1972). [f] H. D. Fleck and E. Parthe, *Acta Crystallogr., Sect. B*, **29**, 1099 (1973). [g] R. Shundles, E. O. Schlemper, and R. K. Murmann, *Inorg. Chem.*, **10**, 2785 (1971).

transition series trivalent and divalent hexaammines, whereas it occurs between $\nu_s(MN)(A_{1g})$ and $\nu_{as}(MN)(F_{1u})$ in the case of hexaammine complexes of trivalent metals belonging to the second and third transition series as well as of hexaammineplatinum(IV). While the frequency ratios $\nu_s(MN)(A_{1g})/\nu_{as}(MN)(F_{1u})$ are nearly constant for all hexaammines, the values for $\nu_s(MN)(A_{1g})/\nu(MN)(E_g)$ and $\nu(MN)(E_g)/\nu_{as}(MN)(F_{1u})$ differ more. If one compares the metal-nitrogen stretching vibrational frequencies for the tetrahedral and square-planar tetraammine complexes of divalent metal ions presented in Tables II and III with those of the hexaammines, it turns out that they occur in the same range as the stretching vibrations of the hexaammines of trivalent metal ions.

Some interesting aspects can be taken from Tables IV and V.

1. The GVFF metal-nitrogen stretching force constants for ammine complexes with the same symmetry, with central atoms having the same oxidation state and belonging to the same transition series, do not differ much.

2. f(MN) increases slightly from $[Mn(NH_3)_6]^{2+}$ to $[Ni(NH_3)_6]^{2+}$ and decreases from the nickel complex to $[Zn(NH_3)_6]^{2+}$. The logarithms of individual stability constants in aqueous solution, which are directly related to the free energies of formation, follow the same trend (Irving-Williams series[39]). The evolution of complexity constants was explained by help of the ligand field theory, which predicts a maximum stabilization for Ni^{2+} and no LFSE for Mn^{2+} and Zn^{2+} octahedral high spin complexes.[40] The estimated bond orders for hexaammine complexes of divalent ions belonging to the first transition series indicate rather little covalent degree. This is confirmed by a comparison of the Co-N bond length in $[Co(NH_3)_6]Cl_2$ with the sums of ionic and covalent radii.

3. The influence of oxidation number on the metal-ligand stretching force constants (and the corresponding vibrational frequencies) is well known for many systems (see ref 41 and literature therein). Bond orders and force constants for hexaammine complexes of trivalent first transition series metal ions are considerably higher compared with those for hexaammines of divalent ions. On going from $[Co(NH_3)_6]^{2+}$ to $[Co(NH_3)_6]^{3+}$, f(MN) is enhanced by more than 130%.

4. As is to be expected for metal-ligand stretching force constants of complexes of transition metals in the same group of the periodic system, f(MN) increases in the series $[Co(NH_3)_6]^{3+}$–$[Rh(NH_3)_6]^{3+}$–$[Ir(NH_3)_6]^{3+}$ and also in the series $[Ru(NH_3)_6]^{3+}$–$[Os(NH_3)_6]^{3+}$ from lighter to heavier central atom. From a comparison of bond lengths and sums of covalent radii as well as from the calculated bond orders, one can see that the hexaammine complexes of trivalent metals belonging to the second and third transition series have nearly purely covalent single bonds. This is also true for the square-planar palladium and platinum complexes. The highest force constant is represented by $[Pt(NH_3)_6]^{4+}$.

5. If the coordination number decreases, the metal-ligand stretching force constant increases (cf. ref 41). This can be seen for the pairs hexaammine- and tetraamminecobalt(II), -zinc, and -cadmium, respectively. Force constants and bond orders for tetrahedral tetraammine complexes of divalent metals and for $[Cu(NH_3)_4]^{2+}$ are of the same order of magnitude as those for hexaammine complexes of trivalent metals of the first transition series.

6. f(MN) for nontransition metal complexes should decrease from the lighter to the heavier central atom of the same group. This is confirmed for tetraamminezinc and -cadmium. The same relation should hold for the corresponding hexaammines, but the force constants for these complexes are not very reliable (see Table I).

According to Bjerrum,[42] the logarithm of the mean complexity constant is a direct measure of the affinity between ammonia and metal ion in aqueous solution. We found a qualitative relation between these data collected from ref 43 and our metal-nitrogen stretching force constants.[44]

Whereas the stretching force constant is a measure of the curvature of the potential function near the equilibrium position, the dissociation energy of a bond is given by the depth of the potential well. Generally, a linear relation between bond energy and stretching force constant is postulated. We could confirm this by comparing our f(MN) values with the total bond energies for the hexaammine complexes of divalent metal ions of the first transition series and for $[Co(NH_3)_6]^{3+}$ determined by a thermodynamic cycle.[45]

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Registry No. $[Mn(NH_3)_6]^{2+}$, 15365-77-2; $[Fe(NH_3)_6]^{2+}$, 15365-76-1; $[Co(NH_3)_6]^{2+}$, 15365-75-0; $[Ni(NH_3)_6]^{2+}$, 15365-74-9; $[Zn(NH_3)_6]^{2+}$, 28074-39-7; $[Cd(NH_3)_6]^{2+}$, 29929-43-9; $[Cr(NH_3)_6]^{3+}$, 14695-96-6; $[Co(NH_3)_6]^{3+}$, 14695-95-5; $[Ru(NH_3)_6]^{3+}$, 18943-33-4; $[Rh(NH_3)_6]^{3+}$, 16786-63-3; $[Os(NH_3)_6]^{3+}$, 48016-91-7; $[Ir(NH_3)_6]^{3+}$, 24669-15-6; $[Pt(NH_3)_6]^{4+}$, 18536-12-4; $[Co(NH_3)_4]^{2+}$, 22580-85-4; $[Zn(NH_3)_4]^{2+}$, 17095-57-7; $[Cd(NH_3)_4]^{2+}$, 18373-05-2; $[Cu(NH_3)_4]^{2+}$, 44001-04-9; $[Pd(NH_3)_4]^{2+}$, 15974-14-8; $[Pt(NH_3)_4]^{2+}$, 16455-68-8.

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Factors Influencing the Structures of Ion Pairs in Solution. Effect of Methyl Substitution in Alkylpyridinium Salts

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A series of paramagnetic anionic lanthanide–nitrato complexes containing *N*-alkyllutidinium cations have been prepared and characterized. The NMR spectra of these complexes in low-dielectric solvents reveal that 3,5 methyl substitution on the pyridine ring alters the structure of the ion pair compared to the previously studied 4-substituted cases, although the interionic distance (7 Å) appears to remain the same. Possible explanations for this phenomenon are considered. Methyl substitution in the 2 or 2,6 positions appears to result in an increase in the interionic distance; this is believed to be a steric effect.

Introduction

Since 1969, the ability of paramagnetic lanthanide ions to influence the NMR chemical shifts of ligand nuclei has found considerable practical application in organic chemistry.[1] In addition to the resolution of complex NMR spectra, lanthanide β-diketonate chelates (shift reagents) have been proven of value in distinguishing between different geometrical optical and conformational isomers of ligand molecules[2-6] and more recently in the extremely complex problem of establishing the conformations of biologically relevant molecules in solution.[7,8]

Applications of such a "shift reagent technique" to the study of the second coordination sphere antedates the development of the lanthanide chelate methods by several years.[9-11] The literature in this area, though not as extensive as in the shift reagent area, has been the subject of several critical reviews.[12]

We have been interested for some time in the use of NMR