electrochemical half-wave potentials, which reflect the energy of a single orbital, show a substantial dependence on ligand structure and correlate well one another. Charge-transfer energies, which reflect a difference in energy between two orbitals, remain approximately constant and do not correlate well with $E_{1/2}$ or binding energy. A similar rationale,[48] citing the spherical component of the ligand field potential as the principal factor determining the energy of a metal orbital, has been proposed to explain the general lack of correlation between $E_{1/2}$ and Dq for transition-metal compounds. A similar argument appears to be applicable in the case of charge-transfer transitions for MoS_8 complexes.

The molecular orbital description of $Mo(H_2dtc)_4^+$ also indicates that the charge donated from ligand to metal, which controls the $E_{1/2}$'s and BE's, does so through Mo–S bonding orbitals that are not involved in the metal-centered redox processes. Thus, large changes in $(E_{1/2})_1$ and $(E_{1/2})_2$ with ligand structure do not necessarily imply substantial ligand character in the electron-transfer act. Finally, the relative constancy of the EPR parameters in Table II indicates that the character of the Mo d_{xy} orbital changes very little as it moves up or down in energy. As demonstrated previously[49] electronic charge and electron spin density are independent properties and may be manifested in different experimental measurements.

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Registry No. $Mo(Et_2dtc)_4PF_6$, 81655-19-8; $[n\text{-}Bu_4N]_3Mo(i\text{-}mnt)_4$, 81643-67-6; $[n\text{-}Bu_4N]_3Mo(ced)_4$, 81642-88-8; $[n\text{-}Pr_4N]_3Mo(ded)_4$, 81642-90-2; $Mo(t\text{-}Butxn)_4^+$, 81625-82-3; $Mo(Et_2dtc)_4^+$, 51155-43-2; $Mo(i\text{-}mnt)_4^{3-}$, 81643-66-5; $Mo(ced)_4^{3-}$, 81642-87-7; $Mo(ded)_4^{3-}$, 81642-89-9; $Mo(ced)_4^{2-}$, 81643-65-4; $Mo(i\text{-}mnt)_4^{2-}$, 81643-64-3; $Mo(ded)_4^{2-}$, 81643-63-2; $Mo(ced)_4^{4-}$, 81643-62-1; $Mo(i\text{-}mnt)_4^{4-}$, 81643-61-0; $Mo(ded)_4^{4-}$, 81643-60-9.

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Nitrogen-14 Nuclear Quadrupole Resonance Spectra of Metal Anthranilate Complexes[1]

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The ^{14}N nuclear quadrupole resonance (NQR) spectra at 77 K have been obtained for solid divalent metal ion complexes ML_2 of the anthranilate anion, $L = CO_2C_6H_4NH_2^-$, where M = Zn, Cd, Hg, Pd(II), Ca, Mg, Ba, Sr, Pb, and Sn(II), and for $Hg(CO_2C_6H_4NH_2)Cl$. The ^{14}N NQR data permit the evaluation of the quadrupole coupling constant $e^2q_{zz}Q/h$ and asymmetry parameter η, the two independent components of the electric field gradient tensor at nitrogen, in all the complexes. The NQR data can be interpreted in terms of a coordinated nitrogen model, on the basis of a modified Townes–Dailey analysis, to yield an estimate of the extent of withdrawal of electronic charge from nitrogen in the metal ion complexes, as compared with that of the protonated amino group as reference compound. The results show that electron withdrawal varies in the order Hg > Pd >> Sn > Pb > Cd ≈ Zn > Ca ≈ Mg > Sr > Ba. The results for the $Hg(CO_2C_6H_4NH_2)_2$ complex are anomalous, suggesting that the electronic environment about nitrogen is different in this complex than that in the others.

Anthranilic acid (*o*-aminobenzoic acid) forms complexes of 2:1 stoichiometry with a variety of divalent metal ions. These complexes have been of interest as potential antiinflammatory drugs, as potential hydrogenation catalysts, as antioxidants in films, and as bond strengtheners in epoxy adhesives.[2-5]

The anthranilate anion acts as a bidendate ligand; coordination occurs through the amino nitrogen and the carboxylato oxygen. The copper[6] and yttrium[7] complexes have been the subjects of crystal structure determinations. In the divalent copper complex the arrangement about the metal center is distorted octahedral. Two anthranilate ligands occupy planar positions in a trans configuration about the metal, while the axial positions are occupied by carbonyl oxygens of the ligands on adjacent complexes. This structure is similar to that found for the glycine–cadmium complex.[8] IR and magnetic measurements suggest that the structures of other bis(anthranilato)metal complexes are similar to that of the copper complex.

The work reported here represents a continuation of previous nuclear quadrupole resonance (NQR) studies of metal–nitrogen interactions.[9-13] Our major concern is to examine the manner in which coordination of the amino group nitrogen to the metal center affects the electron distribution about the

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Table I. Nitrogen Quadrupole Resonance Frequencies (kHz) and EFG Parameters for Metal Anthranilate Complexes $M(CO_2C_6H_4NH_2)_2$[a]

metal	ν_+	ν_-	ν_0	e^2qQ, kHz	η
Sn	2527 (1)	1702 (5)	824 (3)	2753 (4)	0.599
Pb	2613 (1)	1791 (5)	822 (1)	2936 (2)	0.560
Zn	2662 (1)	1862 (1)	800 (1)	3016 (2)	0.531
Cd	2628 (1)	1832 (2)	796 (1)	2973 (2)	0.535
	2594 (1)	1777 (4)	817 (1)	2914 (2)	0.561
Hg	1383 (2)	1106 (2)	277 (3)	1659 (5)	0.334
Hg[b]	1664 (2)	859 (4)	805 (3)	1682 (5)	0.956
Pd	1832 (2)	984 (2)	848 (2)	1877 (4)	0.903
Mg	2969 (1)	2187 (3)	782 (3)	3437 (4)	0.455
Ca	2983 (2)	2146 (5)	837 (2)	3419 (4)	0.490
Sr	2976 (2)	2305 (5)	670 (5)	3521 (7)	0.381
	2940 (2)	2220 (5)	720 (5)	3440 (7)	0.419
Ba	3006 (1)	2311 (4)	695 (1)	3545 (2)	0.392
	2985 (1)	2263 (4)	722 (1)	3499 (2)	0.413

[a] Uncertainties in parentheses. [b] $Hg(CO_2C_6H_4NH_2)Cl$.

nitrogen. As in a previous study of the coordinated amino group,[14] a modified Townes–Dailey analysis is employed to relate the ^{14}N NQR data to the extent of electronic charge removal from the nitrogen upon coordination to the various metal centers. Data are presented for anthranilate complexes of Zn, Cd, Hg, Pd(II), Ca, Mg, Ba, Sr, Pb, and Sn(II), in which all metals are present as divalent metal ions. All of these complexes are diamagnetic; the double-resonance method used to obtain the NQR spectra is not suitable for the study of paramagnetic solids, in which nuclear spin–lattice relaxation is generally rapid.

Experimental Section

Anthranilic Acid–Metal Complexes. Anthranilic acid was obtained from Aldrich Chemical Co. and used without further purification. Metal chlorides of reagent grade quality were used in preparation of the metal complexes.

Bis(anthranilate) complexes of Ca, Mg, Sr, Ba, Sn, Pb, Hg, Cd, Pd, and Zn were prepared in a fashion similar to that reported in the literature.[14] Satisfactory elemental analyses were obtained in all cases.

Mercuric anthranilate chloride, $Hg(C_7H_6NO_2)Cl$, is prepared by stirring a 1:1 mole ratio of anthranilic acid and mercuric chloride in ethanol at 60 °C for 10 h. The mixture is then cooled in an ice bath, after which time a finely divided pink-white solid is isolated by filtration. This material is washed repeatedly with ethanol and water and then dried for 10 h under reduced pressure. Anal. Calcd for $Hg(C_7H_7NO_2)Cl$: C, 22.71; H, 1.64; N, 3.78. Found: C, 22.64; H, 1.75; N, 3.74.

NQR Spectra. All ^{14}N NQR spectra were recorded at 77 K. Samples were generally in the 3–4 g size. A field cycling technique, double-resonance via level crossing (DRLC), was employed to observe the ^{14}N quadrupole transitions. The method has been previously described.[12,15]

Results

The quadrupole resonance frequencies and EFG parameters found for the metal anthranilates are listed in Table I. All but three complexes exhibit only one set of nitrogen absorptions, thereby simplifying the assignment of quadrupole coupling constant (QCC) and asymmetry parameter, η. In the Ba, Sr, and Cd complexes, where two distinct nitrogen environments are present, all six transitions are found; unambiguous determinations of QCC and η values for each nitrogen site were therefore possible in these complexes.

Discussion

To interpret the ^{14}N NQR data, we rely upon a model described earlier.[13] In the metal complexes the immediate environment about N is describable as $C-NH_2M^{2+}$. We assume that the coordination about nitrogen is roughly tetrahedral, with a mirror plane of symmetry as shown in Figure 1. The axes of the electrical field gradient (EFG) tensor are in general not coincident with the molecular axis system, shown in Figure 1 as the primed axes. The angle θ depends on the extent of electron withdrawal from N by M. For example, if M were H^+, the *z* axis would lie along the 3-fold symmetry axis represented by the N–C bond axis.

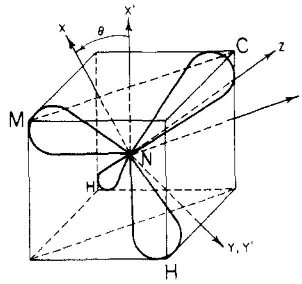

Figure 1. Axis system for the amino nitrogen. The primed axis system (molecular axis) is related to the unprimed axis system (principal axis of the EFG tensor) by a rotation of θ degrees about the $y - y'$ axis, common to both coordinate systems.

We call the nitrogen atomic orbital population in the M–N bond *c*, that in the two N–H bonds *a*, and that in the N–C bond *b*. The EFG parameters are then expressed in terms of these bond populations as in eq 1. Analysis of the ^{14}N NQR

$$\begin{aligned}(q_{zz}/q_0)(1 + \eta) &= \tfrac{3}{4}(b + c - 2a)\\ (q_{zz}/q_0)(1 - \eta/3)\sin 2\theta &= (1/2^{1/2})(b - c) \qquad (1)\\ \cos 2\theta &= (\eta + 1)/(3 - \eta)\end{aligned}$$

data for the metal complexes is best carried out by referring the data to a suitable reference compound. It is most appropriate to choose the zwitterionic form of anthranilic acid, in which the amino nitrogen is protonated. We call the orbital populations in the reference compound a_0, b_0, and c_0, respectively. When one of the protons in $C-NH_3^+$ is replaced by a metal ion upon complex formation, a change in *c*, the nitrogen orbital population in the N–M bond, should result. We expect that $c - c_0$ should be positive. That is, replacement of a proton by a metal ion will in general result in an increased population of the nitrogen donor orbital, because the proton is a stronger Lewis acid than any of the multicoordinated metal ions employed. This change in electron density on nitrogen should induce concomitant smaller changes in the other nitrogen orbital populations. The new populations are given by eq 2. If the nitrogen donor orbital occupation is increased

$$a = a_0 - A(c - c_0) \qquad b = b_0 - B(c - c_0) \qquad (2)$$

upon complex formation as compared with that of the reference, inductive effects should lead to decreases in the nitrogen populations of the orbitals involved in bonding to carbon and the remaining two hydrogens. Thus, the terms that correct for these inductive effects in eq 2 are negative. The quantities *A* and *B* are parametric factors that define the magnitude of the inductive response that causes the *a* and *b* populations to change in response to the change in the *c* population.

We thus have a mathematical expression relating the ^{14}N EFG parameters to relative nitrogen–metal orbital populations. The EFG parameters characteristic of the reference compound are e^2Qq_{zz}/h = 1602 kHz and η = 0.211.[16] By making particular choices for *A* and *B* it is possible to generate graphs of e^2Qq_{zz}/h and η as a function of $c - c_0$. The values of *A* and *B* are chosen to provide a best fit of all the data for the complexes to the model curves. Figure 2 shows the fit for all of the complexes for which the NQR data are reported in Table

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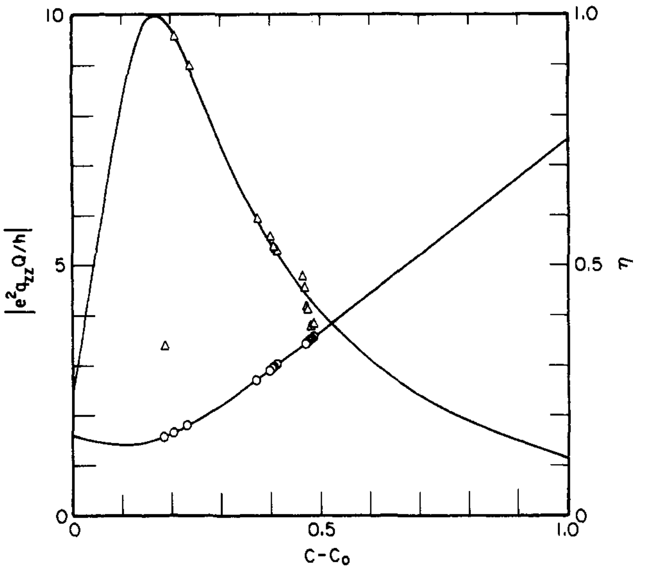

Figure 2. Graphs of e^2Qq_{zz}/h (MHz) and η as a function of $c - c_0$, based on the coordinated nitrogen model, with a zwitterionic form of anthranilic acid as a reference compound. Circles and triangles represent experimental e^2Qq_{zz}/h and η values, respectively.

I, for the case where $A = 0.11$ and $B = 0.26$, which provides the best fit. With the exception of the data for the mercury complex the fit is remarkably good.

The quantity $2A + B$ represents the total inductive response in the other three nitrogen bond orbitals to a unit change in population of the nitrogen orbital directed toward the metal ion. This value for the anthranilate amino group is 0.48, intermediate between that employed in previous work for imidazole–metal binding (0.65)[10] and that employed for the amino–metal interactions in glycine complexes (0.25).[13] The larger inductive responsiveness in the anthranilate case as compared with that of glycine probably results from some measure of π interaction with the phenyl ring to which the amino group is attached. It is worth noting in this connection, however, that moderate variations in the values of A and B only slightly shift the solid lines shown in Figure 2.

Table II lists $c - c_0$ values, the respective nitrogen 1s binding energies obtained from ESCA studies of the anthranilate complexes,[17] and frequencies associated with the N–H stretching modes in the IR spectra of the complexes, obtained as Fluorolube mulls.

Recall that larger $c - c_0$ values represent a lower degree of electron withdrawal from the nitrogen or the metal ion center. The data for the metal complexes seem to fall into three groups: For Ba^{2+}, Sr^{2+}, Mg^{2+}, and Ca^{2+} complexes $c - c_0$ falls in the range 0.49–0.48. For Zn^{2+}, Cd^{2+}, Pb^{2+}, and Sn^{2+} complexes $c - c_0$ falls in the range 0.42–0.39. Finally, for Pd^{2+} and Hg^{2+} complexes $c - c_0$ falls in the range 0.22–0.21. These results show that, as expected, electron withdrawal is greatest for the class B metal ions, i.e., those with larger C/E ratios.[18] There is general agreement with ESCA results relating to nitrogen 1s binding energies, but the NQR-derived parameters show much greater sensitivity to the nature of the metal ion center.

Table II. $c - c_0$ Values, N 1s Binding Energies, and N-H Stretching Frequencies for Complexes $M(CO_2C_6H_4NH_2)_2$

metal	$c - c_0$	N 1s binding energy, eV	N-H str freq, cm^{-1}
Ba	0.490 (4)	399.6	3425 (s), 3382 (m), 3300 (m), 3275 (br)
Sr	0.485 (4)	399.6	3430 (s), 3375 (m), 3302 (m), 3275 (br)
Mg	0.479 (9)	399.7	3317 (s), 3215 (br), 3142 (s)
Ca	0.478 (4)	399.8	3414 (s), 3345 (m), 3300 (m)
Zn	0.424 (4)	399.8	3295 (s), 3230 (br), 3127 (s)
Cd	0.421 (4)	399.8	3287 (s), 3250 (br), 3136 (s)
Pb	0.414 (4)	399.6	3338 (s), 3251 (s)
Sn	0.390 (4)	399.8	3332 (s), 3251 (s)
Pd	0.215 (4)	400.3	3185 (s), 3140 (m), 3105 (s)
Hg[a]	0.205 (4)	...	3265 (s), 3243 (br), 3060 (m)
Hg	...		3035 (s), 2965 (s)

[a] $Hg(CO_2C_6H_4NH_2)Cl$.

There is a slight anomaly in the comparative values for the Mg^{2+} and Ca^{2+} complexes. The value of $c - c_0$ is possibly higher than expected for the magnesium complex because of the steric requirements of the ligand. Mg^{2+} is small, with an ionic radius of only 0.66 Å. Thus, magnesium may not fit as well to the geometrical requirements of the chelating anthranilate ligand as Ca^{2+}, with an ionic radius of 0.99 Å.

The ^{14}N NQR data for the bis(anthranilate) complex of Hg^{2+} exhibit a very poor fit with expectations based on the model. The structure of this complex is not clear. The IR spectra in the N–H stretching region show the N–H stretching modes for this complex to be anomalously low as compared with those of the other complexes (Table II) or anthranilic acid itself in any of its polymorphic forms.[16] The NQR results suggest that the complex has a different structure, involving a substantial departure from the assumed immediate environment about N shown in Figure 1. If this were not so, the ^{14}N data for the complex would fit *somewhere* on the correlation of Figure 2, though possibly not at a value of $c - c_0$ expected for Hg^{2+}.

Ashby and co-workers have applied the model described above to the analysis of the ^{14}N NQR data for amino acid complexes of Zn^{2+} and Cd^{2+}.[13] They obtained $c - c_0$ values in the range from 0.37 to 0.43, in good agreement with the 0.42 obtained for the anthranilate complexes of these two metal ions. In the present work we have been able to extend this model considerably, by employing a wider range of metal ions, thus producing a correspondingly wider range of $c - c_0$ values, from approximately 0.20 to 0.49. The results show that application of the coordinated nitrogen model, with its allowance for an inductive response to electron withdrawal from the nitrogen center, provides a realistic interpretation of the ^{14}N NQR data. The NQR experiment thus provides a sensitive measure of Lewis acidity in metal ion complexes of considerable importance.

Registry No. $Sn(CO_2C_6H_4NH_2)_2$, 23641-87-4; $Pb(CO_2C_6H_4NH_2)_2$, 19022-81-2; $Zn(CO_2C_6H_4NH_2)_2$, 15336-26-2; $Cd(CO_2C_6H_4NH_2)_2$, 5959-14-8; $Hg(CO_2C_6H_4NH_2)_2$, 25427-70-7; $Hg(CO_2C_6H_4NH_2)_2Cl$, 81725-29-3; $Pd(CO_2C_6H_4NH_2)_2$, 41527-17-7; $Mg(CO_2C_6H_4NH_2)_2$, 15336-22-8; $Ca(CO_2C_6Hg_4NH_2)_2$, 74175-22-7; $Sr(CO_2C_6H_4NH_2)_2$, 74175-23-8; $Ba(CO_2C_6H_4NH_2)_2$, 74175-24-9.

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