moment of the right magnitude[20] but does not suit the analytical data so well. Other oxides examined have low magnetic moments (Table IV). The magnetic properties of cobalt and other metallic oxides vary enormously with the method of preparation, physical state, and quantity of water present.[21] The method of preparation of the dark blue substance may be such that magnetically dilute, high-moment hydroxide species are obtained which cannot be reproduced in bulk preparations.

Dark blue "Co(abt)$_2$OH" can be obtained with reasonably reproducible analyses and magnetic and spectral properties by boiling Co(abt)$_2$ in acetone in the air as described. However, aerial oxidation in other conditions, *e.g.*, in acetone or aqueous alkali at room temperature, gives dark blue paramagnetic materials with unreproducible properties. Such variable behavior is indicative of the formation of mixtures.

The reported preparation[5] of diamagnetic Co(abt)$_3$ by reaction between ligand and CoCl$_2$ in aqueous ammoniacal ethanol under nitrogen could not be repeated, and the compound was obtained by reaction in air. The complex is a nonelectrolyte in DMF and has a reflectance spectrum typical of six-coordinate cobalt(III). The two bands in order of increasing energy are assigned to the $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions, respectively.[10a]

The reported preparation[7] of deep blue Cu(abt)$_2$ from direct reaction between ligand and cupric salts in aqueous ethanol seems to be in error. On repeating the preparation, a white mixture of Cu(abt) and (NH$_2$C$_6$H$_4$S)$_2$ was obtained. The cupric ion has oxidized *o*-aminobenzenethiol to the disulfide, yielding a mixture of empirical formula Cu(abt)$_2$. Stabilization of copper(I) by sulfur ligands is well known.[22] The Cu(abt) produced, when present in the mixture or in the pure state, rapidly darkens in air. This probably accounts for the blue color reported for the reaction product. In this case the blue oxidation product has not been identified. Aerial oxidation of cuprous ion and ligand and subsequent oxidation of ligand by cupric ion are all possible so that complex oxidation products are likely with Cu(abt). The ferrous system is similarly complicated.

Further Observations.—The original reports[6,7,18] of Co(abt)$_2$ as low-spin suggested that *o*-aminobenzenethiol should be classified as a high-field ligand. However, in all of the complexes where different spin multiplicities are possible high-spin complexes are formed, except with nickel(II) and cobalt(III). Visible spectra confirm the weak-field nature of the ligand, which on the basis of the spectrum of Co(abt)$_3$ is comparable to water in ligand field strength.

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Deprotonation of *o*-Aminophenol and *o*-Aminothiophenol Complexes of Nickel(II) and Palladium(II)

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In the absence of air, *o*-aminophenol and *o*-aminothiophenol complexes of nickel(II) and palladium(II) are deprotonated by potassium amide in liquid ammonia and form potassium salts of the corresponding anions. These salts react with water to regenerate the parent complexes and with methyl iodide to form S-, O-, and N-methylated derivatives.

o-Aminophenol and *o*-aminothiophenol complexes of the type M(H$_2$NC$_6$H$_4$X)$_2$, where M = Ni, Pd and X = O, S, are well known;[1-5] recently a "metal-stabilized radical–ligand complex" of the composition Ni(H$_2$NC$_6$H$_4$S)$_2$ has been prepared by atmospheric oxidation of bis(*o*-aminothiophenolato)nickel(II) in alkaline solution.[6] Polarographic reduction of this salt in dimethyl sulfoxide and dichloromethane solutions gave evidence for the existence of the bis(*o*-amidothiophenolato)nickelate(II) complex, [Ni(HNC$_6$H$_4$S)$_2$]$^{2-}$, but solid derivatives of this ion were not isolated.[7]

We have found, however, that careful treatment of M(H$_2$NC$_6$H$_4$X)$_2$ complexes with solutions of potassium

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TABLE I

INFRARED SPECTRA IN THE 650–3800-CM^{-1} REGION

$Ni(H_2NC_6H_4O)_2$	$K_2Ni(HNC_6H_4O)_2$	$Pd(H_2NC_5H_4O)_2$	$K_2Pd(HNC_6H_4O)_2$	$Pd(H_2NC_6H_4S)_2$	$K_2Pd(HNC_5H_4S)_2$	Tentative assignments
3310 m	3320 w	3220 m	3280 vw	3190 s	3270 vw	$\nu(NH_2)$, $\nu(NH)$
3260 m		3185 m		3110 s		
3060 m	3055 vw	3070 m	3060 vw	3060 m	3040 vw	$\nu(CH)$
		1693 vw		1692 w		
1600 s		1605 s		1610 s		$\delta(NH_2)$
				1589 s		
1555 m	1568 m	1575 m	1572 m	1545 m	1558 m	
			1558 m			
1487 vs	1490 vs	1485 vs	1485 s	1475 vs	1463 s	$\nu(CC)$
1450 s	1447 m	1452 s	1448 m	1437 m	1433 s	$\nu(CC)$
			1444 m			
	1364 w		1345 m		1348 m	
	1328 w	1330 w		1328 vw	1335 m	
1285 s	1293 m	1303 m	1285 m	1297 m	1295 s	
1264 s	1270 s	1270 s	1268 s	1265 m		
1196 w	1185 w		1210 m	1202 m		
1149 w	1150 w, sh	1150 m	1150 vw	1155 m	1150 w	
	1135 w	1130 m		1125 m		
1110 m	1098 m		1098 m	1107 m, sh	1105 m	
				1064 w	1052 m	
1035 m	1025 m	1031 w	1030 w	1035 m	1022 m	
925 vw	915 w	930 vw	915 vw	934 w		
867 m	875 m	874 m	868 w		840 w	
	788 m	775 m	780 w			
752 s	744 m	748 s	745 m	747 vs	742 m	$\pi(CH)$
733 m, sh					725 m	
				683 m	680 m	$\nu(CS)$

amide in liquid ammonia *with total exclusion of air* readily yields isolatable potassium salts of bis(*o*-amidothiophenolato)palladate(II), bis(*o*-amidophenolato)palladate(II), and bis(*o*-amidophenolato)nickelate(II). Attempts to isolate $K_2[Ni(HNC_6H_4S)_2]$ were thwarted by the extreme solubility of this salt in ammonia.

Experimental Section

Methods and Materials.—Unless otherwise indicated, reactions in liquid ammonia and all physical measurements were performed as described previously.[8] Only standard analytical procedures were employed. Pertinent infrared spectral data are included in Table I; typical spectra are shown in Figure 1. Magnetic moments and X-ray diffraction data are listed immediately following the analytical data.

Bis(*o*-aminophenolato)nickel(II) dihydrate, $[Ni(H_2NC_6H_4O)_2]\cdot 2H_2O$, was prepared by the method of Hieber and Schnackig.[1] *Anal.* Calcd for $[Ni(H_2NC_6H_4O)_2]\cdot 2H_2O$: Ni, 18.9; C, 46.3. Found: Ni, 18.8; C, 46.0. The anhydrous complex was obtained by heating the dihydrate *in vacuo* for 3 hr. *Anal.* Calcd for $[Ni(H_2NC_6H_4O)_2]$: Ni, 21.4. Found: Ni, 21.3. X-Ray diffraction data: 11.32 (1.0), 10.24 (0.5), 3.15 (0.3), 2.22 (0.2). μ_{eff} = 3.2 BM.

Bis(*o*-aminophenolato)palladium(II), $Pd(H_2NC_6H_4O)_2$, was prepared by dissolving 3.0 g of *o*-aminophenol in 80 ml of water containing 0.6 g of NaOH and adding this solution, with stirring, to a solution of 3.26 g of K_2PdCl_4 in 150 ml of water. A reddish brown precipitate formed immediately; after stirring for 5 hr, the mixture was separated by filtration, and the brown solid product was washed with ethanol and ether and dried *in vacuo* over KOH pellets. The yield was 2.65 g or 81% based on K_2PdCl_4. *Anal.* Calcd for $Pd(H_2NC_6H_4O)_2$: Pd, 33.0; C, 44.7; H, 3.75. Found: Pd, 33.2; C, 43.6; J, 3.72. X-Ray diffraction data: 13.08 (0.5), 11.70 (1.0), 4.79 (0.8), 4.23 (0.5), 3.44 (0.5), 3.04 (0.5). This product was diamagnetic.

It has been reported[4] that bis(*o*-aminophenolato)palladium(II) separates as the monohydrate but the samples obtained in this work were anhydrous. No loss of weight or change, either in color or chemical composition, was observed when samples of this complex were heated *in vacuo* for several hours.

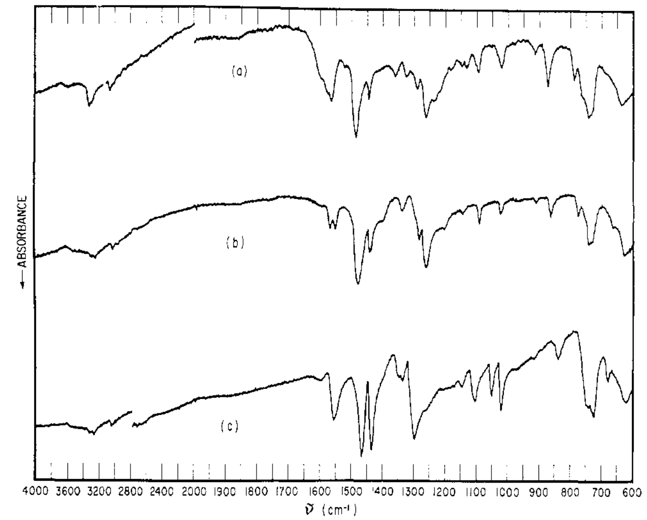

Figure 1.—The infrared spectra of (a) $K_2[Ni(HNC_6H_4O)_2]$, (b) $K_2[Pd(HNC_6H_4O)_2]$, and (c) $K_2[Pd(HNC_6H_4S)_2]$.

Bis(*o*-aminothiophenolato)nickel(II), $Ni(H_2NC_6H_4S)_2$, was prepared by the method of Hieber and Brück.[3] *Anal.* Calcd for $Ni(H_2NC_6H_4S)_2$: Ni, 19.1; C, 46.9. Found: Ni, 19.4; C, 46.9. X-Ray diffraction data: 13.48 (0.9), 4.58 (1.0), 3.50 (0.9), 3.04 (0.8), 2.19 (0.4), 1.69 (0.3). This product was diamagnetic.

Bis(*o*-aminothiophenolato)palladium(II), $Pd(H_2NC_6H_4S)_2$, was prepared as described by Livingstone.[4] *Anal.* Calcd for $Pd(H_2NC_6H_4S)_2$: Pd, 30.0; C, 40.6. Found: Pd, 29.6; C, 40.6. X-Ray diffraction data: 13.59 (1.0), 4.62 (0.8), 4.37 (0.5), 3.47 (0.6), 3.04 (0.3). This product also was diamagnetic.

Preliminary Experiments.—Preliminary experiments were carried out to establish whether the four $M(H_2NC_6H_4X)_2$ complexes would undergo reaction with liquid ammonia. Only in the case

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[8] G. W. Watt and J. F. Knifton, *Inorg. Chem.*, **6**, 1010 (1967).

of bis(*o*-aminothiophenolato)nickel(II) was any significant color change observed when samples of these complexes were exposed to liquid ammonia. To determine whether this was solvation only, a 1.0-g sample of $Ni(H_2NC_6H_4S)_2$ was treated with 30 ml of liquid ammonia for 1 hr and the resulting gray product was separated from the blue supernatant solution by filtration, washed with 20-ml portions of liquid ammonia, and dried *in vacuo*. Infrared spectral and X-ray data for this product were identical with those for the starting material. *Anal.* Found: Ni, 19.5; C, 47.2.

Similar experiments were carried out with the other three complexes, $Pd(H_2NC_6H_4S)_2$, $Pd(H_2NC_6H_4O)_2$, and $Ni(H_2NC_6H_4O)_2$. In each case the products after exposure to ammonia were identical with the starting materials.

Synthesis of Potassium Bis(*o*-amidophenolato)nickelate(II).—To a suspension of 1.14 g of $Ni(H_2NC_6H_4O)_2$ in 30 ml of ammonia at −33.5° was added slowly a solution containing 2.00 molar equiv of KNH_2 in 15 ml of ammonia. After digestion for 3 hr, the black precipitate was separated from the black solution by filtration and washed with two 50-ml portions of ammonia; residual solvent was removed under reduced pressure. *Anal.* Calcd for $K_2[Ni(HNC_6H_4O)_2]$: Ni, 16.7; C, 41.1; H, 2.87. Found: Ni, 16.5; C, 40.3; H, 2.87. X-Ray diffraction data: 12.89 (0.7), 12.02 (1.0), 4.84 (0.8), 3.59 (0.5), 3.29 (0.3), 3.12 (0.3). μ_{eff} = 3.1 BM.

Synthesis of Potassium Bis(*o*-amidophenolato)palladate(II).—A suspension of 0.743 g (2.30 mmol) of $Pd(H_2NC_6H_4O)_2$ in 50 ml of ammonia at −33.5° was treated with a solution containing 2.00 molar equiv of KNH_2 in 14 ml of ammonia. After digestion for 3 hr, the brown precipitate was separated from the dark brown solution by filtration and purified as described above. *Anal.* Calcd for $K_2[Pd(HNC_6H_4O)_2]$: Pd, 26.7; C, 36.1; H, 2.53. Found: Pd, 27.2; C, 35.7; H, 2.61. X-Ray diffraction data: 13.18 (1.0), 4.90 (0.7), 3.56 (0.5), 3.14 (0.3), 2.50 (0.4). This product was diamagnetic.

Synthesis of Potassium Bis(*o*-amidothiophenolato)palladate(II).—A 2.24-g sample of $Pd(H_2NC_6H_4S)_2$ in 50 ml of ammonia was treated with 20 ml of 0.649 *M* KNH_2. The reddish violet solution was stirred for 3 hr without change. Crystallization could be induced only by the removal of at least 50% of the solvent under reduced pressure. The resulting reddish brown crystalline product was separated by filtration and dried *in vacuo* for 24 hr. *Anal.* Calcd for $K_2[Pd(HNC_6H_4S)_2]$: Pd, 24.7; C, 33.4; S, 14.9. Found: Pd, 24.3; C, 33.2; S, 14.8. X-Ray diffraction data: 12.80 (1.0), 5.09 (0.7), 3.65 (0.4), 3.23 (0.4), 2.82 (0.3). This product was diamagnetic.

Reaction of $Ni(H_2NC_6H_4S)_2$ with KNH_2 (1:2).—To 3.01 g of $Ni(H_2NC_6H_4S)_2$ in 30 ml of liquid ammonia was added 20 ml of ammonia containing 2.00 molar equiv of KNH_2. The brown solution was stirred for 3 hr without change. Crystallization could not be induced, either by removal of most of the solvent under reduced pressure or by cooling to −78°. The reaction was repeated using excess KNH_2 and more concentrated solutions of $Ni(H_2NC_6H_4S)_2$ in ammonia, but in no case was it possible to isolate a solid product except by evaporating the reaction mixture to dryness.

Reactions of $K_2[M(HNC_6H_4X)_2]$ Complexes with Water.—The $K_2[M(HNC_6H_4X)_2]$ complexes isolated in this work appear stable in a dry helium atmosphere but rapidly absorb moisture on exposure to air. The parent complexes may be regenerated from the potassium salts by treatment with water. In one such experiment, a 0.5-g sample of $K_2[Pd(HNC_6H_4S)_2]$ was added to 50 ml of cold water and the mixture was stirred for 30 min. The dark brown solid product was filtered off, washed with water, ethanol, and ether, and dried *in vacuo* over KOH pellets. Infrared spectral and X-ray diffraction data for this product were identical with those for $Pd(H_2NC_6H_4S)_2$. *Anal.* Found: Pd, 29.8; C, 39.8.

Reactions of $K_2[M(HNC_6H_4X)_2]$ Complexes with Methyl Iodide.—In a typical experiment, 25 ml of freshly distilled CH_3I was added to a 0.5-g sample of $K_2[Pd(HNC_6H_4S)_2]$ by distillation under reduced pressure, and the mixture was stirred for 7 days at 25°. After removal of excess CH_3I by filtration, the remaining reddish brown solid was washed with water (to remove KI) and recrystallization from ethanol. *Anal.* Calcd for $Pd(H_3CHNC_6H_4SCH_3)I_2$: Pd, 20.7; N, 2.73; S, 6.24. Found: Pd, 20.4; N, 2.67; S, 6.66. X-Ray diffraction data: 8.18 (0.9), 6.06 (0.7), 5.53 (1.0), 4.28 (0.5), 3.52 (0.6), 2.36 (0.5).

Methylation of $K_2[Pd(HNC_6H_4O)_2]$ was effected in the same manner by treatment with excess CH_3I for 3 days in the absence of air and recrystallization of the product from methanol. *Anal.* Calcd for $[Pd(CH_3HNC_6H_4OCH_3)I_2]$: Pd, 21.4; C, 19.3; H, 2.23; N, 2.81. Found: Pd, 21.2; C, 19.8; H, 2.52; N, 2.07.

Similarly, treatment of $K_2[Ni(HNC_6H_4O)_2]$ with CH_3I yielded crude products the infrared spectra of which exhibited a number of characteristic CH_3 absorption bands. However, the instability of these N-methylated derivatives in a variety of solvents prevented the isolation of a pure product.

Discussion

Treatment of the *o*-aminophenol complexes of nickel(II) and palladium(II) and the *o*-aminothiophenol complex of palladium(II) with potassium amide in liquid ammonia with complete exclusion of air has been shown to result in deprotonation and formation of the potassium salts of the corresponding anions, thus

$$Pd(H_2NC_6H_4S)_2 + 2KNH_2 \longrightarrow K_2[Pd(HNC_6H_4S)_2] + 2NH_3 \quad (1)$$

$$Pd(H_2NC_6H_4O)_2 + 2KNH_2 \longrightarrow K_2[Pd(HNC_6H_4O)_2] + 2NH_3 \quad (2)$$

$$Ni(H_2NC_6H_4O)_2 + 2KNH_2 \longrightarrow K_2[Ni(HNC_6H_4O)_2] + 2NH_3 \quad (3)$$

The identity of these complexes has been confirmed by analysis, infrared spectral studies, and, in the cases of the potassium bis(*o*-amidothiophenolato)palladate(II) and potassium bis(*o*-amidophenolato)palladate(II) complexes, by the formation of methylated derivatives. In addition, it has been demonstrated that the parent compounds, $M(H_2NC_6H_4X)_2$, may be regenerated from their deprotonated derivatives, $K_2[M(HNC_6H_4X)_2]$, by treating samples of the latter with water. Significantly, these reprotonation reactions readily take place without the use of even mild oxidizing or reducing conditions, as might be necessary had the metal ions in these deprotonated complexes not been in the 2+ oxidation state.

Attempts were made to prepare derivatives of bis(*o*-aminothiophenolato)nickel(II) but, under the conditions employed, it was not possible to isolate any useful product owing to the high solubility of the reaction products in liquid ammonia. There is no reason to believe, however, that the $Ni(HNC_6H_4S)_2^{2-}$ species is not formed *in situ*. Stability constant data, in particular, indicate[9] that for this type of chelate, the sulfur rather than the oxygen analog is capable of forming the more stable complex with nickel(II).

The magnetic properties of the $K_2[M(HNC_6H_4X)_2]$ complexes are essentially the same as their precursors and it would appear that fundamental changes in the environment of the nickel and palladium ions in these species do not take place during deprotonation. Apparently, following proton abstraction, the increase in charge density about the coordinated nitrogen atoms of the $M(HNC_6H_4X)_2^{2-}$ species is reduced by π bonding

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(9) R. G. Charles and H. Freiser, *J. Am. Chem. Soc.*, **74**, 1385 (1952).

in the *o*-amidophenol and *o*-amidothiophenol ligands, rather than by ligand-to-metal electron transfer.

Additional information concerning the $K_2[M(HNC_6H_4X)_2]$ complexes was sought from studies of their vibrational spectra. Unfortunately, however, the value of these data was severely limited by the difficulty in correlating the rather complicated spectra of the deprotonated and parent materials with the considerable number of active vibrational modes of the chelated *o*-aminophenol and *o*-aminothiophenol ligands. In the absence of theoretical calculations, only a few of the observed bands could be confidently assigned on an empirical basis. All of the spectra of the $K_2[M(HNC_6H_4X)_2]$ complexes were consistent with deprotonation at the coordinated amino group.

In agreement with previous assignments for the free *o*-aminophenol and *o*-aminothiophenol ligands,[10,11] the NH_2 stretching and bending modes were identified in the spectra of the $M(HNC_6H_4X)_2$ complexes with the bands between 3325 and 3195 cm^{-1} and at *ca.* 1600 cm^{-1}. The singlet centered around 1600 cm^{-1} does not appear in the spectra of the deprotonated species. Similarly, the series of bands between 3325 and 3195 cm^{-1} are reduced to a weak singlet [owing to the ν(NH) mode] in the spectra of the $K_2[M(HNC_6H_4X)_2]$ complexes. A number of other bands also exhibited by the parent complexes either disappear or are of reduced intensity in the spectra of their deprotonated derivatives, and these too are probably due to NH_2 bending modes.

The spectrum of the methylated derivative $Pd(H_3CHNC_6H_4SCH_3)I_2$ exhibits a number of new bands which are not present in the spectrum of either $Pd(H_2NC_6H_4S)_2$ or $K_2[Pd(HNC_6H_4S)_2]$. Those at 3000 (m) and 2925 (m), 1481 (s), 1418 (m), and 1398 (m), and 990 (m), 966 (s), and 910 (m) cm^{-1} are typical of the CH_3 stretching, bending, and rocking vibrations.[12,13] Similar bands were also observed in the spectrum of $Pd(CH_3HNC_6H_4OCH_3)I_2$.

The formation of $Pd(CH_3HNC_6H_4SCH_3)I_2$ by treatment of $K_2[Pd(HNC_6H_4S)_2]$ with CH_3I is certainly not without precedent. Busch, *et al.*, have reported[14] that bis(β-mercaptoethylamine)palladium(II) combines with CH_3I in dimethylformamide solution to yield the S-methylated complex $Pd(H_2NCH_2CH_2SCH_3)I_2$. A similar methylation involving ligand displacement[15] takes place upon treatment of deprotonated bis(β-mercaptoethylamine)palladium(II) with CH_3I. In each of these reactions the characteristic ligand displacement which accompanies S and N methylation can only be attributed to the weak coordinating ability of the thioether[16] and substituted amino[17] groups.

Methylation and reprotonation reactions such as those described above help to establish the relationship between the $K_2[M(HNC_6H_4X)_2]$ complexes and their fully protonated counterparts, $M(H_2NC_6H_4X)_2$. An oxidation–reduction relationship has also been shown to exist between the $M(HNC_6H_4X)_2^{2-}$ species and the "metal-stabilized radical–ligand complex," $Ni(HNC_6H_4S)_2$, mentioned earlier. Holm, *et al.*, have reported[7] that a two-electron reduction of this material in dimethyl sulfoxide and dichloromethane solutions provides the $Ni(HNC_6H_4S)_2^{2-}$ complex. The same complexes may also be usefully compared in terms of their stability in different basic media.

The formation of $Ni(HNC_6H_4S)_2$ by atmospheric oxidation of $Ni(H_2NC_6H_4S)_2$ in aqueous alkaline solution[7] must, at some stage, involve proton abstraction from the coordinated *o*-aminothiophenol ligands. A similar deprotonation reaction with $Ni(H_2NC_6H_4S)_2$ in liquid ammonia, but in the complete absence of air, might well yield an analogous Ni(II)-deprotonated species, but our experiments prove that all of the $M(H_2NC_6H_4X)_2$ complexes studied in this work are stable under these conditions. Only upon treatment with strongly basic solutions of potassium amide in liquid ammonia has it been possible to generate the $M(HNC_6H_4X)_2^{2-}$ species.

It may be concluded that only when the oxidation state of the nickel and palladium ions is $>2+$ can the metal ion stabilize the coordinated *o*-amidophenol and *o*-amidothiophenol ligands in aqueous alkali or liquid ammonia solutions. It requires far more basic reaction conditions to form a stable nickel(II)–amido ligand or palladium(II)–amido ligand complex. This is consistent with previous studies[18] and with the conclusion[19] that, in general, the acidic properties of the coordinated amino group depend upon the charge and size of the central metal ion.

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