singlet–triplet splittings from magnetic susceptibility and magnetization studies on triplet-state systems have large ranges of uncertainties.

I have remeasured the magnetic susceptibility of a powdered sample of $[Cu(dedtc)_2]_2$ in the temperature range 4.2–27.3 K and have compared the data obtained for this study with data reported in 1971 by Villa and Hatfield.[5] Data in this temperature range should be most sensitive to changes in state populations. There is very good agreement between the data obtained earlier in my laboratory and the new data with the expected field dependence being observed.[6]

Exchange Coupling in the Triplet Ground State Molecule Bis(μ-pyridine *N*-oxide)bis[bis(nitrato)(pyridine *N*-oxide)copper(II)]. Pyridine *N*-oxide complexes of copper(II) salts have long been of interest.[71-73] A structural determination of the parent member of the series, $[Cu(pyNO)Cl_2]_2$,[74] revealed that the copper(II) ions were bridged by pyridine *N*-oxide ligands. Watson and co-workers[75,76] reviewed the structure and magnetic data available in 1969 for pyridine *N*-oxide complexes of copper(II) salts and commented on the existence of dimeric complexes with normal magnetic moments.

The compound of immediate interest here is $[Cu(pyNO)_2(NO_3)_2]_2$, which is known from single-crystal X-ray diffraction structural studies to have the dimeric, parallel-planar structure shown in Figure 1.[77] Each plane consists of mutually trans-coordinated pyridine *N*-oxide and nitrato ligands with short copper–oxygen bonds (1.94–1.98 Å) with the long out-of-plane bond being 2.439 Å, and the Cu–O–Cu′ bridge angle is 102.9°.[77]

Subsequently, crystals of the mixed-metal system $[Cu_xZn_y(4\text{-R-pyNO})_4(NO_3)_4]$ (R = H, CH_3, OCH_3) were studied by EPR spectroscopy,[14] and triplet-state lines were observed in the half-field region, in the low-field parallel region (near 2260 G), and in a high-field region near 3500 G). Hyperfine structure was observed on the half-field and fine-structure lines of $[Cu(pyNO)_2(NO_3)_2]_2$ present in a matrix of predominantly diamagnetic $[Zn(pyNO)_2(NO_3)_2]_2$. Relatively intense lines from $[CuZn(pyNO)_4(NO_3)_4]$ obscured a portion of the triplet-state spectrum, but careful manipulation of rotation spectra of single crystals permitted an examination of important features of the triplet spectra. The triplet-state spectra were analyzd in terms of the spin Hamiltonian

$$\mathcal{H}_{S'} = g_{\parallel}\mu_B H_z S_z' + g_{\perp}\mu_B(S_x'H_x + S_y'H_y) + D(S_z'^2 - 2/3) + A(S_{1z}I_{1z} + S_{2z}I_{2z}) + B(S_{1x}I_{1x} + S_{1y}I_{1y} + S_{2x}I_{2x} + S_{2y}I_{2y})$$

with the spin Hamiltonian parameters $g_{\parallel} = 2.275$ (5), $g_{\perp} = 2.07$ (1), $|D| = 0.073$ (1) cm^{-1}, $|A| = 0.0130$ (2) cm^{-1}, and $|B| = 0.0040$ (4) cm^{-1}. Comparable spectra and spin Hamiltonian parameters were obtained for the 4-methylpyridine *N*-oxide analogue. Although the EPR spectra for the 4-methoxypyridine *N*-oxide analogue were less well resolved, the half-field line at about 1600 G was clearly visible.[14]

Magnetic susceptibility and magnetization studies have been carried out on $[Cu(4\text{-R-pyNO})_2(NO_3)_2]_2$, where R = H, CH_3, and OCH_3.[14] Since the triplet state and exchange coupling were known from EPR studies to be extant in these complexes, the magnetic susceptibility and magnetization data were analyzed in terms of singlet and triplet states. The data for $[Cu(pyNO)_2(NO_3)_2]_2$ and $[Cu(4\text{-MepyNO})_2(NO_3)_2]_2$ revealed positive exchange-coupling constants and triplet ground states, while the data for the methoxypyridine *N*-oxide analogue were consistent with a single ground state.

There is additional experimental evidence for the continuum in exchange coupling from positive to negative exchange-coupling constants as measured by singlet–triplet splittings. Kahn and co-workers[78,79] have shown that it is possible to design systems with $J_{AF} = 0$ (see eq 5) and in this manner have measured $J = J_F = J_{max}$.

The various terms that contribute to the singlet–triplet splitting in dimeric copper(II) acetate monohydrate as a result of exchange coupling have been considered recently in an ab initio calculation by de Loth et al.[80] These authors present a development of superexchange interactions introduced by Anderson[81] as well as higher order contributions including polarization of the ligands and closed shells. Summation of the various terms involved in the exchange process leads to a singlet–triplet splitting consistent with that which is experimentally observed. An examination of the rigorous ab initio development provides further support for the thesis of this note.

Experimental Section

Magnetic susceptibility data were collected on a powdered sample of $[Cu(dedtc)_2]_2$ with use of a Princeton Applied Research Model 155 vibrating-sample magnetometer and procedures that have been described elsewhere.[82]

Acknowledgment. This research was supported by the National Science Foundation through Grant CHE 80 09685.

Registry No. $[C_4(pyNO)_2(NO_3)_2]_2$, 26507-58-4; $[Cu(dedtc)_2]_2$, 33939-19-4.

Supplementary Material Available: Listings of structural and magnetic properties of bis(μ-hydroxo)- (Table I), bis(μ-chloro)- (Table II), and sulfur-bridged copper(II) compounds (Table III) (4 pages). Ordering information is given on any current masthead page.

---

(71) Quagliano, J. V.; Fujita, J.; Franz, G.; Phillips, D. J.; Walmsley, J. A.; Tyree, S. Y. Jr. *J. Am. Chem. Soc.* **1961**, *83*, 3770–3773.

(72) Hatfield, W. E.; Muto, Y.; Jonassen, H. B.; Paschal, J. S. *Inorg. Chem.* **1965**, *4*, 97–99.

(73) Hatfield, W. E.; Morrison, J. C. *Inorg. Chem.* **1966**, *5*, 1390–1394.

(74) Schafer, H. L.; Morrow, J. C.; Smith, H. M. *J. Chem. Phys.* **1965**, *42*, 504–508.

(75) Watson, W. H. *Inorg. Chem.* **1969**, *8*, 1879–1886.

(76) Kidd, M. R.; Watson, W. H. *Inorg. Chem.* **1969**, *8*, 1886–1891.

(77) Ščavničar, S.; Matković, B. *Acta Crystallogr., Sect. B* **1969**, *B25*, 2046–2055.

(78) Kahn, O.; Galy, J.; Tola, P.; Coudanne, H. *J. Am. Chem. Soc.* **1978**, *100*, 3931.

(79) Kahn, O.; Claude, R.; Coudane, H. *J. Chem. Soc., Chem. Commun.* **1978**, 1012.

(80) de Loth, P.; Cassoux, P.; Daudey, J. P.; Malrieu, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 4007–4016.

(81) Anderson, P. W. *Solid State Phys.* **1963**, *14*, 99–214.

(82) Corvan, P. J.; Estes, W. E.; Weller, R. R.; Hatfield, W. E. *Inorg. Chem.* **1980**, *19*, 1297–1300.

Contribution from the Department of Chemistry,
Utkal University, Bhubaneswar 751004, India

Kinetics and Mechanism of the Complex Formation between Aluminum(III) and Some (Salicylato)pentaamminecobalt(III) Ions

Anadi C. Dash

Received March 22, 1982

Previous studies have dealt with the kinetics of the reversible formation of the binuclear species of Fe(III) with (oxalato)pentaamminecobalt(III)[1] ($(NH_3)_5CoO_2CCO_2Fe^{4+}$) and (salicylato)pentaamminecobalt(III)[2] ions ($N_5CoO_2CC_6H_4OFe^{4+}$; $N_5 = 5\ NH_3$, $(en)_2(NH_3)$, and tetraethylenepentamine). Evidence has been presented that supports our earlier views that Fe^{3+} is chelated by the oxalate and salicylate

---

(1) Dash, A. C.; Harris, G. M. *Inorg. Chem.* **1982**, *21*, 1265.

(2) Dash, A. C.; Harris, G. M. *Inorg. Chem.* **1982**, *21*, 2336.

0020-1669/83/1322-0837$01.50/0 © 1983 American Chemical Society

Table I. Rate Data for the Complexation of Aqueous Al(III) with $(NH_3)_5CoO_2CC_6H_3(X)OH^{2+}$ [a]

X	$-\log [H^+]$ ($\pm$0.03)	$10^3[Al^{3+}]_T$, M	10^2k_{obsd}, s^{-1}	$10^3[Al^{3+}]_T$, M	10^2k_{obsd}, s^{-1}	$10^3[Al^{3+}]_T$, M	10^2k_{obsd}, s^{-1}	10^3k_r, s^{-1}	k_f, $M^{-1}s^{-1}$
H	2.28	3.62	0.88 ± 0.04	7.24	1.00 ± 0.15	10.9	1.08 ± 0.08	7.74 ± 0.09	0.29 ± 0.03
		14.5	1.21 ± 0.12						
	2.53	3.62	1.10 ± 0.10	7.24	1.31 ± 0.10	10.9	1.42 ± 0.08	9.8 ± 0.4	0.39 ± 0.04
		14.5	1.54 ± 0.10						
	2.73	3.62	1.30 ± 0.03	7.24	1.71 ± 0.13	10.9	1.80 ± 0.03	9.9 ± 0.8	0.80 ± 0.08
		14.5	2.20 ± 0.03						
	3.03	3.62	1.83 ± 0.09	7.24	2.11 ± 0.11	10.9	2.4 ± 0.2	14.7 ± 0.7	0.92 ± 0.09
		14.5	2.9 ± 0.2						
	3.22	3.02	2.8 ± 0.4	6.04	3.3 ± 0.3	9.06	3.5 ± 0.3	24.8 ± 1.4	1.2 ± 0.2
		12.1	4.0 ± 0.4						
5-NO_2	2.28	3.62	0.765 ± 0.005	7.24	0.87 ± 0.04	10.9	1.00 ± 0.02	6.6 ± 0.2	0.28 ± 0.03
		14.5	1.03 ± 0.03						
	2.53	3.62	0.90 ± 0.02	7.24	1.04 ± 0.02	10.9	1.12 ± 0.02	8.0 ± 0.2	0.30 ± 0.02
		14.5	1.24 ± 0.02						
	2.73	3.62	0.96 ± 0.01	7.24	1.09 ± 0.08	10.9	1.19 ± 0.05	8.3 ± 0.2	0.36 ± 0.05
		14.5	1.53 ± 0.13						
	3.03	3.62	1.33 ± 0.04	7.24	1.55 ± 0.10	10.9	1.82 ± 0.05	10.1 ± 0.9	0.82 ± 0.09
		14.5	2.28 ± 0.06						
	3.22	3.02	1.67 ± 0.11	6.04	2.07 ± 0.16	9.06	2.21 ± 0.10	13.7 ± 0.9	1.0 ± 0.1
		12.1	2.61 ± 0.10						
3-NO_2	2.28	3.62	0.45 ± 0.02	7.24	0.51 ± 0.03	10.9	0.55 ± 0.04	4.0 ± 0.1	0.12 ± 0.02
		14.5	0.58 ± 0.04						
	2.47	3.62	0.46 ± 0.01	7.24	0.52 ± 0.02	10.9	0.56 ± 0.02	4.1 ± 0.1	0.13 ± 0.01
		14.5	0.61 ± 0.02						
	2.73	3.62	0.49 ± 0.02	7.24	0.54 ± 0.02	10.9	0.59 ± 0.02	4.4 ± 0.1	0.14 ± 0.01
		14.5	0.64 ± 0.02						
	2.96	3.62	0.53 ± 0.02	7.24	0.57 ± 0.02	10.9	0.63 ± 0.02	4.7 ± 0.2	0.16 ± 0.02
		14.5	0.70 ± 0.02						
	3.22	3.02	0.62 ± 0.04	6.04	0.75 ± 0.03	9.06	0.82 ± 0.03	5.4 ± 0.1	0.30 ± 0.04
		12.1	0.90 ± 0.06						

[a] Conditions: $I = 0.1$ M; temperature 29.0 ± 0.1 °C; $[Co(III)]_T = (2.5\text{–}7.4) \times 10^{-4}$ M.

moieties already bound to the cobalt(III) center.[3] In the consideration of the thermodynamic stabilities[3b,4] of the binuclear species formed by Al(III) with (salicylato)pentaamminecobalt(III) ($N_5CoO_2CC_6H_3(X)OAl^{4+}$; $N_5 = 5\ NH_3$, X = H; $N_5 = (en)_2(NH_3)$, X = H, 5-SO_3^-, 5-NO_2, 5-Br, 3-NO_2) and of the effectiveness of Al(III) in promoting water for (salicylato)aluminum(III) substitution[3b] at the cobalt(III) center, it was presumed that this metal ion is also chelated by the cobalt(III)-bound salicylate moieties cited above. Martin and Gould[5] also have postulated the formation of a chelated intermediate between Ti(III) and (salicylato)pentaamminecobalt(III) prior to the electron-transfer process. Data on the kinetics of the formation of such binuclear species of Al(III) are at present not available, though some studies have been made of the formation kinetics of monosalicylato Al(III) complexes.[6,7] This paper deals with studies of the kinetics of the reversible complexation of Al(III) with some substituted (salicylato)pentaamminecobalt(III) ions, which provide insight into the mechanism of the formation and dissociation of the binuclear product species.

Experimental Section

Materials and Method. Substituted (salicylato)pentamminecobalt(III) perchlorates $[(NH_3)_5CoO_2CC_6H_3(X)OH](ClO_4)_2$ (X = H, 5-NO_2, 3-NO_2) were prepared by known procedures:[8,9] λ_{max} (nm; ϵ, $M^{-1}\ cm^{-1}$) = 505 (79.0), 505 (77.7), and 505 (77.0) for salicylato, 5-nitrosalicylato, and 3-nitrosalicylato cobalt(III) complexes, respectively, in 0.01 M $HClO_4$ medium, which agrees well with the previously reported values.[2,9] The samples were analyzed for cobalt, which agreed within 0.1% of the calculated value. An aluminum(III) perchlorate solution was prepared and analyzed for aluminum(III) and the free acid content as described earlier,[3] the stock solution ($[Al^{3+}]_T$ = 0.805 M, $[HClO_4]$ = 0.619 M) had sufficient acid to prevent hydrolysis and polymerization of $Al(OH_2)_6^{3+}$. The ionic strength of the reaction mixture was adjusted with sodium perchlorate. Sodium chloroacetate–chloroacetic acid buffer was used to control the pH of the reaction medium. pH measurements were made with a digital pH meter, Model 5651, manufactured by the Electronic Corporation of India. A Beckman DU2 UV–visible spectrophotometer was used for spectral measurements.

Rate Measurements. The kinetics of complexation of $(NH_3)_5CoO_2CC_6H_3(X)OH^{2+}$ with Al(III) was investigated at 29.0 ± 0.1 °C and I = 0.1 M. The rate measurements were made at 330, 380, and 390 nm for salicylato, 5-nitrosalicylato, and 3-nitrosalicylato complexes, respectively, where an appreciable increase of absorbance was observed with time when the reactants were mixed. In a typical kinetic run 3 mL of a solution containing aluminum(III) perchlorate, sodium perchlorate, and the buffer was equilibrated in a pair of 10-mm matched quartz cells in the thermostated cell compartment of the Beckman DU2 spectrophotometer. A freshly prepared solution of the complex (0.005–0.012 M) was also brought to thermal equilibrium separately, and 0.2 mL of this solution was added to the reaction mixture carefully. Rapid mixing of the complex was effected by inverting the Teflon-stoppered cell several times. This took ~15 s, after which absorbance readings were taken at the preset wavelength. The optical density scale was set initially to the absorbance of the cobalt(III) complex. For the faster reactions (completion time <180 s) the cell containing the reaction mixture was kept in the light path and the photo tube was exposed to the transmitted light; the meter deflection was zeroed by operating on the absorbance knob at known time intervals. Thus it was possible to record the absorbance at 5-s intervals after the initial delay time stated above. The concentration of the cobalt(III) complex was chosen such that the initial absorbance (A_0, due to the complex only) was between 0.2 and 0.4 unit. The absorbance at infinite time (A_∞), which varied with pH and $[Al^{3+}]_T$ for a given complex (A_∞ was steady for a given run) concentration, was 0.1–0.4 unit higher than A_0 for most runs except for the runs with the salicylato complex at $[Al^{3+}]_T = 3.62 \times 10^{-3}$ M (pH 2.28 and 2.53), for which it was 0.06 unit. Runs were made under pseudo-first-order conditions with $[complex]_T = (2.5\text{–}7.4) \times 10^{-4}$ M and with $[Al^{3+}]_T$ and pH as specified in Table I. The observed pseudo-first-order rate constants were calculated from the slope of

---

(3) (a) Dash, A. C.; Nanda, R. K. *Inorg. Chem.* **1974**, *13*, 655. (b) Dash, A. C.; Nanda, R. K. *Ibid.* **1973**, *12*, 2024.

(4) Dash, M. S.; Dash, A. C. *J. Inorg. Nucl. Chem.* **1976**, *38*, 571.

(5) Martin, A. H.; Gould, E. S. *Inorg. Chem.* **1976**, *15*, 1934.

(6) Secco, F.; Venturini, M. *Inorg. Chem.* **1975**, *14*, 1978.

(7) Perlmütter-Hayman, B.; Tapuhi, E. *Inorg. Chem.* **1979**, *18*, 875.

(8) Gould, E. S.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1318.

(9) Nanda, R. K.; Patnaik, H. K. *J. Indian Chem. Soc.* **1976**, *53*, 431.

Table II. Kinetic Parameters for the Formation and Dissociation of $(NH_3)_5CoO_2CC_6H_3(X)OAl^{4+}$

X	k_1, M^{-1} s^{-1}	$10^4k_2K_1$, s^{-1}	k_2, M^{-1} s^{-1}	10^3k_{-1}, s^{-1}	$10^6k_{-2}K_2$, s^{-1} M	k_{-2},[a] s^{-1}	k_2/k_1	k_{-2}/k_{-1}
H	0.16 ± 0.06	7.4 ± 1.6	67 ± 15	5.9 ± 0.3	9.4 ± 1.2	9.4	418	1593
5-NO_2	0.14 ± 0.03	5.2 ± 0.8	47 ± 7	6.0 ± 0.4	4.5 ± 0.8	4.5	335	750
3-NO_2	0.10 ± 0.01	0.9 ± 0.2	8 ± 2	3.84 ± 0.03	0.95 ± 0.03	0.95	82	247

[a] Based on $K_2 = 10^{-6}$ M.

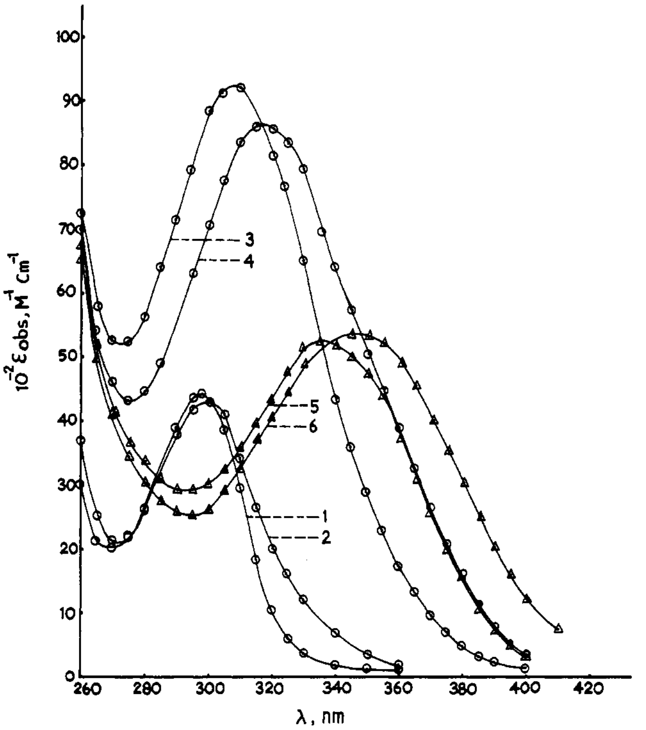


Figure 1. Spectra of $(NH_3)_5CoO_2CC_6H_3(X)OH^{2+}$ ($10^{-2}\epsilon_{obsd}$, M^{-1} cm^{-1} vs. λ, nm) in the presence and absence of Al(III), at pH 3.18 and 29 °C: (1) X = H, (3) X = 5-NO_2, (5) X = 3-NO_2, cobalt(III) substrates only; (2) X = H, (4) X = 5-NO_2, (6) X = 3-NO_2, cobalt(III) substrates + Al(III), $[Co(III)]_T/[Al^{3+}]_T = 1/100$.

ln ($A_\infty - A_t$) vs. time (s) plots and are reported (see Table I) as the mean of triplicate runs.

Results and Discussion

The spectra of the cobalt(III) complexes in the absence and presence of Al(III) ($[complex]_T/[Al^{3+}]_T = 1/100$, pH 3.18) are presented in Figure 1. The interaction of Al^{3+} with $(NH_3)_5CoO_2CC_6H_3(X)OH^{2+}$ is accompanied by the spectral shift as follows: λ_{max} (nm; ε, M^{-1} cm^{-1}) 298 (4431) → 300 (4282) (X = H); 308 (9250) → 318 (8625) (X = 5-NO_2); 337 (5250) → 348 (5350) (X = 3-NO_2). This may be taken as evidence in favor of the formation of the binuclear species $(NH_3)_5CoO_2CC_6H_3(X)OAl^{4+}$. Table I presents the observed pseudo-first-order rate constants as a function of total aluminum(III) concentration and pH at 29 °C and $I = 0.1$ M. A few runs were made with the 5-nitrosalicylato complex at constant $[Al^{3+}]_T$ ($=10.9 \times 10^{-3}$ M) and pH ($=3.03$; $I = 0.1$ M) and under varying concentrations of the buffer. The values of 10^2k_{obsd} (s^{-1}) obtained are 1.80 ± 0.05, 1.82 ± 0.05, 1.78 ± 0.03, 1.80 ± 0.03, and 1.84 ± 0.06 at $[A]_T$ ($=[ClCH_2CO_2H] + [ClCH_2CO_2^-]$) values of 0.021, 0.028, 0.035, 0.044, and 0.0525 M, respectively. This indicated that the buffer effect is negligible. Secco and Venturini[6] have also reported in their study of the formation of the monosalicylato Al(III) complex that chloroacetate buffer is inert to Al^{3+} ions in an aqueous medium.

One notes that the observed rate constants fit the equation (1) at a fixed pH and varying Al(III) concentrations. The

$$k_{obsd} = k_f[Al^{3+}] + k_r \qquad (1)$$

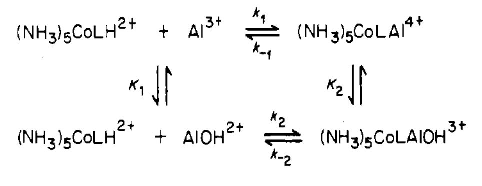
slope and the intercept of the straight-line plot of k_{obsd} vs. $[Al^{3+}]_T$ at each pH are identified with the pseudo-first-order rate constants for the formation (k_f) and the dissociation (k_r) of the binuclear species at that pH, respectively. Furthermore, both the slopes and the intercepts of such plots when plotted against $[H^+]^{-1}$ yield straight lines with positive intercepts and slopes, indicating thereby that the formation as well as dissociation of $(NH_3)_5CoO_2CC_6H_3(X)OAl^{4+}$ occurs via two pathways: one independent of $[H^+]$ and another dependent on $[H^+]^{-1}$. Over the experimental pH range, the (salicylato)cobalt(III) substrates will exist in the phenol form ($pK_{OH} > 7$).[4,10,11] It is, therefore, reasonable to assume that the inverse hydrogen ion dependence results from the reaction of $Al(OH_2)_5(OH)^{2+}$ with $[(NH_3)_5CoO_2CC_6H_3(X)OH]^{2+}$ and the dissociation of the binuclear hydroxoaluminum(III) species $[(NH_3)_5CoO_2CC_6H_3(X)OAlOH]^{3+}$, respectively. The overall scheme for the formation/dissociation of the binuclear species may, therefore, be represented as shown in Scheme I (proton dissociation occurs in the direction of the arrows adjacent to each dissociation constant), and H^+-catalyzed dissociation of the binuclear species $(NH_3)_5CoLAl^{4+}$ is not detectable under the present experimental conditions.[12] The hydrolysis constant of $Al(OH_2)_6^{3+}$ (K_1) is 1.1×10^{-5} M at 29 °C and $I = 0.1$ M,[13] and the value of K_2 is likely to be less than that of K_1 due to the influence of the negative charge of the phenoxide ion in $(NH_3)_5CoO_2CC_6H_3(X)OAl^{4+}$.[14] With these facts taken into consideration, the components of k_{obsd} as defined by eq 1 are given by eq 2 and 3. The values of k_f and k_r obtained as the

$$k_f = k_1 + k_2K_1/[H^+] \qquad (2)$$

$$k_r = k_{-1} + k_{-2}K_2/[H^+] \qquad (3)$$

least-squares slopes (S) and intercepts (I)[15] of k_{obsd} vs. $[Al^{3+}]_T$ plots at fixed pH values are given in Table I. The rate parameters (k_1, k_2K_1 and k_{-1}, $k_{-2}K_2$) were then calculated by

Scheme I



LH = $^-O_2CC_6H_3(X)OH$; X = H, 5-NO_2, 3-NO_2

---

(10) Dash, A. C.; Nanda, R. K.; Patnaik, H. K. *Transition Met. Chem. (Weinheim, Ger.)* **1977**, *2*, 183.

(11) A value of 8.06 ± 0.03 was obtained for the pK_{OH} of $[(NH_3)_5CoO_2CC_6H_3(5\text{-}NO_2)OH]^{2+}$ ($I = 0.1$ M, 29 °C) when the observed molar extinction coefficients (ϵ_{obsd}) of this complex (at 400 nm) in imidazole buffer of pH 6.09–8.33 were fitted to the relationship $K_{OH} = [H^+](\epsilon_{obsd} - \epsilon_2)/(\epsilon_1 - \epsilon_{obsd})$, where $\epsilon_1 = 15\,280$ M^{-1} cm^{-1} and $\epsilon_2 = 114$ M^{-1} cm^{-1}, the molar extinction coefficients of the phenoxide and phenol forms of the complex, respectively.

(12) Similar observations have been made with $(NH_3)_5CoO_2CCO_2Fe^{4+}$ and $(NH_3)_5CoO_2CC_6H_4OFe^{4+}$.[1,2] For the latter, however, acid-catalyzed dissociation is detectable at $[H^+] > 0.2$ M.

(13) Schofield, R. K.; Taylor, A. W. *J. Chem. Soc.* **1954**, 4445.

(14) As, for example, the pK of $Al(OH_2)_5(OH)^{2+}$ is 0.6 unit higher than that of $Al(OH_2)_6^{3+}$ at 25 °C and $I = 0.1$ M (see: "Critical Stability Constants"; Smith, R. M.; Martell, A. E., Eds.; Plenum Press: New York, 1976; Vol. 4, p 11).

(15) k_{obsd} values were weighted inversely as the square of the errors quoted.

fitting the k_f and k_r data at different [H^+] values to eq 2 and 3, respectively.[16] One notes from the values of k_1 and k_2 (see Table II) that the rates of formation of the binuclear species $(NH_3)_5CoO_2CC_6H_3(X)OAl^{4+}$ are only slightly dependent on the nature of the substituent X on the aromatic ring. The relatively slow rate of complexation of the 3-nitrosalicylato cobalt(III) substrate particularly in the k_2 path presumably reflects that intramolecular hydrogen bonding between the phenolic group and the vicinal NO_2 group makes the cobalt(III)-bound 3-nitrosalicylate ligand less reactive.

A comparison of the values of k_1 and k_2 with the rate data for the formation of monosalicylato Al(III)[6] and mono-5-nitrosalicylato Al(III)[7] complexes via the reactions $Al^{3+} + HL^- \rightarrow AlL^+$ ($k \cong 1$ M^{-1} s^{-1} at 25 °C, $I = 0.1$ M) and $AlOH^{2+} + HL^- \rightarrow AlL^+$ ($k \cong 2 \times 10^3$ M^{-1} s^{-1} at 25 °C, $I = 0.1$ M) reveals that the coordinated ligands react ~10 times slower in the k_1 path and ~100 times slower in the k_2 path. Similar rate differences have also been observed in the complexing of Fe(III) by (oxalato)pentaamminecobalt(III) and (salicylato)pentaamminecobalt(III) substrates.[1,2] Perlmütter-Hayman and Tapuhi[7] reported a value of $<8 \times 10^{-3}$ M^{-1} s^{-1} for the rate constant of the complexation of 5-nitrosalicylic acid with Al(III) at 25 °C and $I = 0.1$ M. The value of k_1 (0.14 M^{-1} s^{-1}) obtained in the present work for the corresponding cobalt(III) substrate reduces to 4.7×10^{-3} M^{-1} s^{-1} at $I = 0$.[17] The values of k_1 for the cobalt(III) substrates are ~100 times smaller than the most recent data for the water-exchange rate constant of $Al(OH_2)_6{}^{3+}$ ($=k_{ex} = 16$ s^{-1} at 25 °C).[18] A similar observation has been made in the study of the kinetics of complexation of (salicylato)pentaamminecobalt(III) ions with Fe^{3+}, for which $k_1 = 7 \pm 2$ M^{-1} s^{-1} (30 °C, $I = 1.0$ M)[2] and $k_{ex}(Fe(OH_2)_6{}^{3+}) = 160$ s^{-1} (25 °C).[19] The fact that $k_1 < k_{ex}$ eliminates the simple S_N2 mechanism concept and supports an I mechanism. For the substitution reactions of $Fe(OH_2)_6{}^{3+}$, the I_a mechanism[1,2,20] has been proposed. Such a possibility cannot be ruled out[21] completely for $Al(OH_2)_6{}^{3+}$ though, according to Swaddle,[22] substitution at $Al(OH_2)_6{}^{3+}$ will have more of the I_d character. Much faster substitution reactions for $Al(OH_2)_5(OH)^{2+}$, as observed in the present work, are consistent with the I_d mechanism as has been proposed for $Fe(OH_2)_5(OH)^{2+}$.[1,2,20,23]

The binuclear species $(NH_3)_5CoO_2CC_6H_3(X)OAl^{4+}$ undergo spontaneous dissociation at rates ($k_{-1} = (5.9–3.8) \times 10^{-3}$ s^{-1}) comparable with the rate of spontaneous dissociation of the monosalicylato Al(III) complex ($k = 7.9 \times 10^{-3}$ s^{-1}; 25 °C, $I = 0.1$ M)[6] and 100 times slower than that of the (salicylato)pentaamminecobalt(III)–Fe(III) complex.[2] So that the nature of the binuclear species could be elucidated, a few trial experiments were also made to see if *p*-nitrophenol could complex with Al(III) under the experimental conditions employed in the present work. There was, however, no spectrophotometric evidence for the interaction of *p*-nitrophenol with Al(III). These facts, therefore, suggest that the binuclear species of Al(III) resemble structurally their (salicylato)aluminum(III) analogues (i.e., the salicylate moieties of the cobalt(III) substrates chelate Al(III) with deprotonation of the phenol group). The opening up of the chelate ring (carboxylate end) is most likely the rate-controlling step in the dissociation. With the assumption[24] that $K_2 = 10^{-6}$ M, the values of the dissociation rate constants (k_{-2}) of $[(NH_3)_5CoO_2CC_6H_3(X)OAlOH]^{3+}$ have been calculated (see Table II). A marked labilizing action of the hydroxo group ($k_{-2}/k_{-1} \cong 10^2$) is also evident in the dissociation reaction of the binuclear species.

Registry No. Al, 7429-90-5; $[(NH_3)_5CoO_2CC_6H_4OH]^{2+}$, 30931-74-9; $[(NH_3)_5CoO_2CC_6H_3(5\text{-}NO_2)OH]^{2+}$, 56295-01-3; $[(NH_3)_5CoO_2CC_6H_3(3\text{-}NO_2)OH]^{2+}$, 60552-07-0.

---

[16] k_f and k_r were weighted as $1/\sigma^2(S)$ and $1/\sigma^2(I)$, respectively.

[17] $\log k_I = \log k_0 + 1.02Z_AZ_B(I^{1/2}/(1 + I^{1/2}))$: Eyring, H.; Lin, S. H.; Lin, S. M. "Basic Chemical Kinetics"; Wiley: New York, 1980; p 414.

[18] "Coordination Chemistry-II"; A. E. Martell, Ed.; American Chemical Society: Washington, DC, 1978; ACS Monogr. No. 174, Table 1-1, p 5.

[19] Grant, M.; Jordan, R. B. *Inorg. Chem.* **1981**, *20*, 55.

[20] Hasinoff, B. B. *Can. J. Chem.* **1976**, *54*, 1820; **1979**, *57*, 77.

[21] The exchange rate of $M(OH_2)_6{}^{3+}$ (M = Al(III), Ga(III), In(III)) is suggested not to involve a simple dissociative mechanism (see ref 18, p 18).

[22] Lo, S. T. D.; Swaddle, T. W. *Inorg. Chem.* **1975**, *14*, 1878.

[23] Mentasti, E.; Secco, F.; Venturini, M. *Inorg. Chem.* **1982**, *21*, 602.

[24] $K_2/K_1 = 0.1$ is a reasonable estimate.[14]

Contribution from the Department of Chemistry,
Texas Woman's University, Denton, Texas 76204

Improved Method for the Preparation of Pentafluorosulfur Bromide

Rahim Rahbarnoohi and Lewis C. Sams*

Received February 3, 1982

Pentafluorosulfur bromide is a particularly attractive reagent for the addition of the SF_5 group into other compounds,[1–4] but its use is limited because its synthesis is inefficient. Procedures for its synthesis have been described by Merrill[1] (low yield) and by Cohen and MacDiarmid[5] (low conversion). Kovacina, Berry, and Fox[6] described a procedure in which the bromine, recovered from the reaction with S_2F_{10}, was returned to the reactor with additional S_2F_{10}, giving yields that increased from 46% in the first reaction to above 80% in the fourth and further reactions.

In this note we report two simple modifications of the Kovacina, Berry, and Fox method that will permit yields of high-purity SF_5Br exceeding 80% (based on S_2F_{10} charged) from the first synthesis, thereby eliminating the necessity of having low yields in the first three reactions. Using the Fox fractionation procedure (traps at −78, −116, and −196 °C) we found from the ^{19}F NMR spectra that SF_5Br was distributed among three collection traps, indicating that improvements need to be made in the fractionation procedure. Our improvements allow SF_5Br to be isolated in 85% yield in the first synthesis.

The S_2F_{10} and purified bromine were obtained from Professor G. Gard of Portland State University and J. T. Baker Chemical Co., respectively. The ^{19}F NMR spectra were obtained with a Varian EM-390 NMR spectrometer operated at 85 MHz with SF_6 as the reference.

In the repetition of Fox's procedure 10 mmol of S_2F_{10} and 100 mmol of Br_2 were heated in a 300-mL Monel cylinder at 150 °C for 16 h. The cylinder was evacuated while being held at liquid-nitrogen temperature, the liquid nitrogen was poured out of the Dewar, and the cool Dewar was placed around the cylinder. The trap-to-trap fractionation (−78, −116, and −196

---

[1] C. Merrill, paper presented at the 3rd International Symposium on Fluorine Chemistry, Munich, Aug 1965.

[2] J. Stewart, L. Kegley, H. F. White, and G. Gard, *J. Org. Chem.*, **34**, 760 (1969).

[3] A. D. Berry and W. B. Fox, *J. Fluorine Chem.*, **6**, 175 (1975).

[4] T. Kitazume and J. M. Shreeve, *J. Am. Chem. Soc.*, **100**, 492 (1978).

[5] B. Cohen and A. G. MacDiarmid, *Inorg. Chem.*, **4**, 1782 (1965).

[6] T. A. Kovacina, A. D. Berry, and W. B. Fox, *J. Fluorine Chem.*, **7**, 430 (1976).

0020-1669/83/1322-0840$01.50/0