Cobalt(III) Complexes with Quadridentate Ligands. IX.[1] High-Resolution Solid-State ^{13}C CP/MAS NMR Spectra of the Salicylato-, Carbonato-, Dichloro-, and Dinitro(quadridentate amine)-cobalt(III) Complexes

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Synopsis. High-resolution solid-state ^{13}C CP/MAS NMR was applied to many cobalt(III) complexes, such as salicylato-, carbonato-, dichloro-, and dinitro(quadridentate amine)cobalt(III) complexes, $[CoL_2(\text{quadridentate amine})]^+$ (L: 1/2sal, $1/2CO_3$ Cl, NO_2; quadridentate amine: tren, trien, 2,3,2-tet, 3,2,3-tet, 3,3,3-tet). The signals of the methylene carbons of the coordinated quadridentate amine ligands in their complexes have been assigned to the center, NH_2- side, NH- side, and N- side methylene carbons. Also, the signals of the ring carbons of the coordinated salicylato ligand in their complexes have been assigned to the individual carbon atoms. It has been found that the signals of nonprotonated carbons (C-1, C-2, and C-7) of the coordinated salicylato ligand have been very high and that the ^{13}C CP/MAS NMR method is well-suited for studies of unstable compounds in solutions.

In the last decade, the high-resolution solid-state ^{13}C CP/MAS NMR method has been extensively applied to various organic materials.[2] This method has been proven to give very usuful information about the molecular structure and conformation of organic compounds,[3] the molecular motion of polymers,[4] and the rate processes in solids.[5] However, this method has not yet been adequately applied to the field of metal complexes. The present paper deals with the assignments of the ^{13}C NMR signals of the quadridentate amine and the ring carbons of the salicylato of $[CoL_2(\text{quadridentate amine})]^+$ (L: 1/2sal, $1/2CO_3$, Cl, NO_2; quadridentate amine: tren, trien, 2,3,2-tet, 3,2,3-tet, 3,3,3-tet) and deals with the application of the ^{13}C CP/MAS NMR method.

Experimental

Measurements. The ^{13}C CP/MAS NMR measurements were performed on a Bruker MSL high-power spectrometer operating at a field strength of 4.7 T, equipped with a double bearing (DB-MAS) and a variable-temperature probe unit. The resonance frequency was 50.323 MHz. A contact time of 2 ms was chosen, and the repetition time was 5 s. The 90° pulse width was typically 4 us for both ^{13}C and ^{1}H under cross-polarization conditions. The spectral width and data points were 30 kHz and 8 K points respectively. The spectra were usually obtained by the accumulation of from 300 to 500 FIDs, thus achieving a resonable signal-to-noise ratio for natural abundance samples. The ^{13}C chemical shifts were calibrated indirectly through external glycine-CO (δ=176.03; line width=15 Hz) relative to tetramethylsilane. The experimental errors of the ^{13}C chemical shift values were estimated to be within ±0.2 ppm. The alumina rotor with samples was spun at a rate of from 2500 to 3500 Hz with compressed dry air. Samples of ca. 150—250 mg were packed in the rotor. The ^{13}C NMR spectra in solutions were recorded with an FX-60 spectrometer (JEOL).

Preparation of Complexes. The $[Co(CO_3)(tren)]Cl \cdot 1.5H_2O$ (**1**), $[CoCl_2(tren)]Cl \cdot H_2O$ (**6**), $[Co(NO_2)_2(tren)]Cl$ (**11**), *cis*-α-$[Co(CO_3)(trien)]ClO_4 \cdot H_2O$ (**2**), *cis*-β-$[Co(CO_3)(trien)]Cl \cdot 1.5H_2O$ (**3**), *cis*-α-$[CoCl_2(trien)]Cl$ (**7**), *cis*-β-$[CoCl_2(trien)]Cl \cdot 0.5H_2O$ (**8**), *cis*-α-$[Co(NO_2)_2(trien)]Cl \cdot H_2O$ (**12**), *cis*-β-$[Co(NO_2)_2(trien)]NO_3$ (**13**), *cis*-β-$[Co(CO_3)(2,3,2\text{-tet})]Cl$ (**4**), *trans*-$[CoCl_2(2,3,2\text{-tet})]Cl \cdot 2.5H_2O$ (**9**), *cis*-β-$[Co(CO_3)(3,2,3\text{-tet})]Cl \cdot 3H_2O$ (**5**), and *trans*-$[CoCl_2(3,2,3\text{-tet})]Cl \cdot H_2O$ (**10**) were prepared according to previously published procedures.[6]

The *t*-$[Co(sal)(tren)]Cl \cdot H_2O$ (**14**), *p*-$[Co(sal)(tren)]Cl \cdot H_2O$ (**15**), *cis*-β_1-$[Co(sal)(trien)]Cl \cdot H_2O$ (**16**), *cis*-β_2-$[Co(sal)(trien)]Cl \cdot H_2O$ (**17**), *cis*-β_1-$[Co(sal)(2,3,2\text{-tet})]Cl \cdot H_2O$ (**18**), *cis*-β_2-$[Co(sal)(2,3,2\text{-tet})]Cl \cdot 2H_2O$ (**19**), *cis*-β_2-$[Co(sal)(3,2,3\text{-tet})]Cl \cdot 3H_2O$ (**20**), and *cis*-β_2-$[Co(sal)(3,3,3\text{-tet})]Cl \cdot H_2O$ (**21**) were also prepared according to previously published procedures.[7]

Abbreviations: tren: tris(2-aminoethyl)amine; trien: triethylenetetramine; 2,3,2-tet: 3,7-diazanonane-1,9-diamine; 3,2,3-tet: 4,7-diazadecane-1,10-diamine; 3,3,3-tet: 4,8-diazaundecane-1,11-diamine.

Results and Discussion

The coordinated quadridentate amine ligands of **1—3** exhibit the two ^{13}C CP/MAS NMR signals of the methylene carbons at δ=42—47 and 53—58, as is shown in Fig. 1. The signals at δ=42.2 and 56.3 of **1** have been assigned to the NH_2- side ($NH_2\mathbf{C}H_2\mathbf{C}H_2N$-) and N- side methylene carbons ($NH_2CH_2\mathbf{C}H_2N$-) respectively of the coordinated tren ligand. The signals at δ=43—47 and 53—58 of **2** and **3** have been assigned to the NH_2- side and NH- side methylene carbons ($NH_2\mathbf{C}H_2\mathbf{C}H_2NH\mathbf{C}H_2$-) respectively. The signal of the NH_2- side methylene carbons of **2** is different from that of **3**; i.e., it is due to the configurations of cis-α and cis-β. The complexes **4** and **5** exhibit three signals of the methylene carbon at δ=22—29, 39—46, and 49—58. The signals at δ= 39—46 and 49—58 were assigned to the NH_2- side and NH- side methylene carbons respectively by comparison with those of **1—3**. Accordingly, the signals at δ=22—29 are assigned to the center methylene carbons ($NH_n\mathbf{C}H_2\mathbf{C}H_2\mathbf{C}H_2NH$-, *n*: 1 or 2) of the coordinated quadridentate amine ligands. The signals of **3—5** are difficult to assign to the individual carbon atoms. However, the signals at δ=49.9 of **4** and at δ=49.8 of **5** are assigned to C-4 and C-6, and C-3 and C-7, methylene carbons[7c] respectively, because their methylene carbons are neighboring carbons of the center methylene carbons of C-2, C-5, or C-8. The signals at δ=

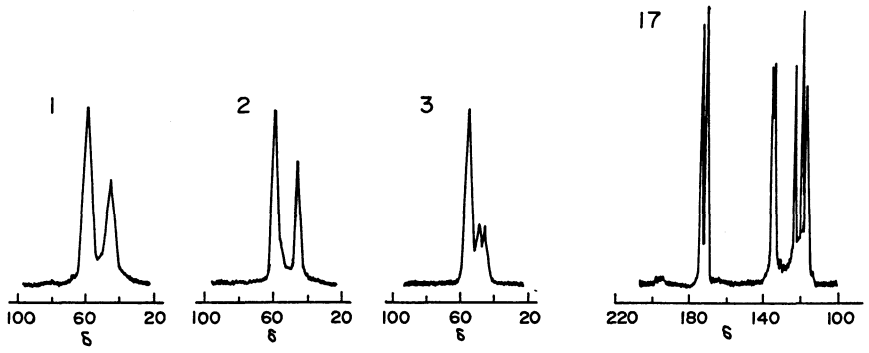

Fig. 1. The ^{13}C CP/MAS NMR spectra of complexes **1**—**3** and **17**.
1: $[Co(CO_3)tren]Cl \cdot H_2O$. **2**: *cis*-α-$[Co(Co(CO_3)trien]ClO_4 \cdot H_2O$.
3: *cis*-β-$[Co(CO_3)trien]Cl$. **17**: *cis*-β_2-$[Co(sal)trien]Cl \cdot H_2O$.

Table 1. ^{13}C CP/MAS NMR Spectra of **1**—**21**, and ^{13}C NMR Spectra of **1**, **3**—**6**, and **9**—**13** in D_2O

Complex No.	Center carbons δ	NH_2- side carbons δ	NH- (or N-) side carbons δ				CO_3 δ	Salicylato δ						
			C-3,	C-7	C-4,	C-6		C-1	C-2	C-3	C-4	C-5	C-6	C-7
1		42.2		(56.3)			170.4							
2		43.8		57.4			166.5							
3		44.1 46.7		53.7			167.1							
4	23.5	42.7	57.2		49.9		167.7							
5	22.9 28.9	39.8 45.1	49.8		53.8		166.7							
6		47.2		(64.1)										
7		45.7		55.9										
8		43.1 48.3		53.2										
9	29.3	45.5	55.4		49.9									
10	27.7	39.8	48.6		54.5									
11		46.2		(59.2 62.0)										
12		44.0		[54.5 58.2 59.2 60.5]										
13		43.7 48.5		[51.7 53.0]										
14		45.8		(60.9)				120.5	169.8	117.2	134.3	126.1	134.3	172.4
15		44.4		(60.1)				114.8	168.9	114.8	133.1	125.0	133.1	171.2
16		43.2[a]		51.6[a]				117.4	168.4	117.4	133.4	121.6	133.4	172.9
17		40.6[a]		52.2[a]				118.4	167.0	116.3	134.9	122.7	133.8	172.6
18	23.6	43.6[a]		50.5[a]				116.0	169.9	114.3	132.0	124.6	132.0	171.2
19	21.6	45.5[a]		52.1[a]				121.3	168.7	116.9	132.7	123.7	132.7	172.9
20	20.8 27.8	44.6[a]		47.6[a]				118.0	167.5	114.9	135.5	123.0	132.1	171.5
21	23.5	37.4[a]		48.2[a]				116.2	167.9	116.2	123.7	123.4	132.7	170.6
1		42.9		(53.5 55.8)			172.7							
3		42.4 47.4	[50.9 51.4	52.6 52.9]			167.4							
4	23.7	43.3 44.0	[47.2 50.4	50.9 56.0]			168.9							
5	22.2 27.0	39.7 40.1	[46.7 48.7	50.5 54.4]			168.0							
6		45.4 46.6		(61.2 63.0)										
9	28.8	43.3	55.6		49.1									
10	27.7	39.8	49.4		53.3									
11		45.2		(61.0 63.1)										
12		42.6		[55.5 57.5]										
13		42.9 47.0	[50.7 51.5	53.1 53.7]										

quadridentate amine

Standards: Glycine δ=42.9 and 43.8 for CH_2, δ=176.03 for ^{13}CO for solid-states; internal dioxane (δ=67.4) for solutions.
[ ]: The chemical shifts could not be assigned to the individual methylene carbon. a) Broad signal.

166—171 of **1**—**5** have been assigned to the coordinated carbonato carbons. The signals of the center, NH_2- side, NH- side, and N- side methylene carbons of the coordinated quadridentate amine ligands in **6**—**13** were assigned by comparison with those of **1**—**5**; these results are collected in Table 1. The signals at δ=20—28, ca. 37—46, ca. 47—53, and 60—61 of **14**—**21** were assigned to the center, NH_2- side, NH- side, and N- side methylene carbons of the coordinated quadridentate amine ligands respectively

by comparison with those of **1**—**13**. The salicylato carbon signals in the regions at δ=114—173 of the coordinated salicylato ligand have been assigned to the individual carbon atoms by comparison with those of **14**—**17**[7a,b] in solution; these results are collected in Table 1.

The chemical shifts of the center, NH_2- side, NH- side, and N- side methylene carbons of the coordinated quadridentate amine ligands of **1**—**13** are almost the same as those of **14**—**21**, and their chemical shifts are close to those in solutions, as is shown in Table 1 and Ref. 7. The methylene carbon signals can be affected by the electronic effect, the steric effect, the coordination number, or the configuration of the coordinated ligands in complexes; e.g., the NH_2- side and N- side methylene carbon signals of **1** appear at a higher field than those of **6** and **11**. The NH- side methylene carbon signals of **12** and **13** are very different from those of Complexes **2** and **3** and Complexes **7** and **8**. Also, the spectrum of **3** is different from that of **2**.

A difference between the ^{13}C CP/MAS NMR method and the ^{13}C NMR method was found in the signals of nonprotonated carbon and the measurements of unstable compounds in solutions: the signals of the C-1, C-2, and C-7 carbons (nonprotonated carbons) of the coordinated salicylato ligand have been very high, such as C-3, C-4, C-5, and C-6 carbons (protonated carbons), as is shown in Fig. 1. The ^{13}CNMR spectra of **2**, **7**, and **8** did not show the expected signals in solution, since they were changed to other species;[6b] e.g., the spectrum of **7** in solution is in agreement with that of $[Co(H_2O)_2(trien)]^{3+}$ (**22**). Also, the spectrum of **18**[7c] has not showed the expected signals, because **18** isomerizes to **19** in solution.

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