

which is attributable to antisymmetric angle deformations. The band is significantly split, an observation contrary to that observed for the noncoordinated example; the splitting is less than that observed for unidentate or bidentate coordination. Thus, unfortunately, the infrared data do not rule out bidentate perchlorate bonding, but the nature of the spectral features does seem to discount the possibility. The crystal structure of this complex is currently under investigation in our laboratories.

Note Added in Proof. Complete structural details for $[\text{Cu}(\text{bipy})\text{OH}]_2(\text{ClO}_4)_2$ are now available [M. Toofan, A. Boushehri, and M. Haque, *J. Chem. Soc., Dalton Trans.*, 217 (1976)]. The refined structural results reveal that the Cu–O–Cu angle, ϕ , is 96.94° , and that the perchlorate ion is coordinated in the bidentate manner described for α - $[\text{Cu}(\text{dmaep})\text{OH}]_2(\text{ClO}_4)_2$. The new value for ϕ gives a $2J$ prediction of $+45 \text{ cm}^{-1}$. The more positive experimental value of $+93 \text{ cm}^{-1}$ deviates from the linear relationship in the same manner that has been noted for α - $[\text{Cu}(\text{dmaep})\text{OH}]_2(\text{ClO}_4)_2$, that is, $2J$ was predicted to be -50 cm^{-1} while the experimental value was found to be -4.8 cm^{-1} .

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Registry No. $[\text{Cu}(\text{tmen})\text{OH}]_2(\text{ClO}_4)_2$, 14266-63-8; $[\text{Cu}(\text{tmpd})\text{OH}]_2(\text{ClO}_4)_2$, 59532-73-9.

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Chelation in Organoaluminum–Nitrogen Chemistry¹

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The various factors affecting the formation and stability of neutral, chelated four-coordinate organoaluminum–nitrogen compounds have been investigated. A variety of new compounds have been prepared and fully characterized. Cryoscopic molecular weight data suggest the predominant species to be the chelated monomer for the compounds $(\text{CH}_3)_2\text{Al}(\text{C}_2\text{H}_5)_2\text{NC}_2\text{H}_4\text{N}(\text{C}_2\text{H}_5)_2$, $(\text{C}_2\text{H}_5)_2\text{Al}(\text{CH}_3)\text{NC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, $(\text{C}_6\text{H}_5)_2\text{Al}(\text{C}_2\text{H}_5)\text{NC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, $\text{Cl}_2\text{Al}(\text{C}_2\text{H}_5)\text{NC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, and $(\text{CH}_3)_2\text{AlSC}_2\text{H}_4\text{N}(\text{CH}_3)_2$. At lowered temperatures, NMR studies and additional molecular weight data suggest that an equilibrium exists between the monomeric chelate and a dimer. Other compounds such as $(\text{CH}_3)_2\text{Al}(\text{CH}_3)\text{NC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, $(\text{CH}_3)_2\text{Al}(\text{CH}_3)\text{NC}_3\text{H}_6\text{N}(\text{CH}_3)_2$, and $(\text{C}_2\text{H}_5)_2\text{Al}(\text{CH}_3)\text{NC}_3\text{H}_6\text{N}(\text{CH}_3)_2$ show a significant concentration of the dimeric species at room temperature. The dimer molecule can exist in cis and trans conformations relative to the nitrogen of the four-membered ring. In all cases observed, the cis isomer is preferred. An unusual observation is that $[(\text{CH}_3)_2\text{Al}(\text{CH}_3)\text{NC}_2\text{H}_4\text{N}(\text{CH}_3)_2]_2$ is present as only the cis isomer at low temperature. Many factors are shown to affect the position of the monomer–dimer equilibrium. These include steric effects of groups bound to aluminum, steric effects of groups bound to potentially bridging and terminal nitrogens of the ligand, ligand base strength, and chelate ring size. There is also evidence that the mechanism of formation may affect chelation and association.

Introduction

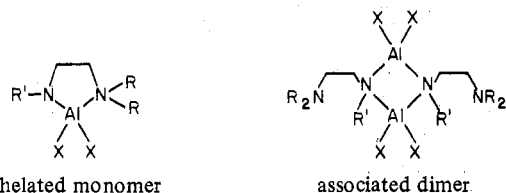
The reaction of an organoaluminum compound with a Lewis base containing an acidic hydrogen such as $\text{N}(\text{CH}_3)_2\text{H}$ results in the formation of a derivative of the aluminum compound such as $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$ and an alkane. Many of these aluminum derivatives have been found to be associated by bridging through the base group. The degree of association

is variable and often not readily predictable. Several factors including electronic effects, steric effects, thermodynamic effects, and the mechanism of formation are considered to play important roles in determining the extent of these associations.^{2–4} Compounds of this type which have bidentate ligands also have an unpredictable degree of association. Chelated monomers have been observed in the case of $(\text{CH}_3)_2\text{Al}$

Table I. Synthesis and Properties of Compounds

Compd	Reaction conditions	Purification methods	Physical properties at room temp
$H_2Al(CH_3)NC_2H_4N(CH_3)_2$	Diethyl ether, 25 °C for 1 h	Vacuum sublimn, 50 °C	Colorless crystals, mp 75–83 °C
$H_2Al(C_2H_5)NC_2H_4N(CH_3)_2$	Diethyl ether, 25 °C for 1 h	Vacuum sublimn, 50 °C	Colorless crystals, mp 117–119 °C
$(CH_3)_2Al(CH_3)NC_2H_4N(CH_3)_2$	Sealed tube, 100 °C for 24 h	Short-path vacuum distilln, ~55 °C	Colorless liq
$(CH_3)_2Al(C_2H_5)NC_2H_4N(C_2H_5)_2$	Sealed tube, 100 °C for 24 h	Short-path vacuum distilln, ~50 °C	Colorless liq
$(CH_3)_2Al(CH_3)NC_3H_6N(CH_3)_2$	Sealed tube, 100 °C for 24 h	Short-path vacuum distilln, ~70 °C	Colorless liq
$(C_2H_5)_2Al(CH_3)NC_2H_4N(CH_3)_2$	Sealed tube, 120 °C for 24 h	Short-path vacuum distilln, ~60 °C	Colorless liq
$(C_2H_5)_2Al(CH_3)NC_3H_6N(CH_3)_2$	Sealed tube, 120 °C for 24 h	Short-path vacuum distilln, ~65 °C	Colorless liq
$(CH_3)_3AlOC_2H_4N(CH_3)_2$	Toluene, 25 °C for 1 h	Vacuum sublimn, 80 °C	Colorless crystals, mp 125–127 °C
$(CH_3)_2AlSC_2H_4N(CH_3)_2$	Toluene, 25 °C for 1 h	Vacuum sublimn, 50 °C	Colorless crystals, mp 65–67 °C
$(C_6H_5)_2Al(C_2H_5)NC_2H_4N(CH_3)_2$	Sealed tube, 120 °C for 24 h	Vacuum sublimn, 90 °C	Colorless crystals, mp 107–108 °C
$Cl_2Al(C_2H_5)NC_2H_4N(CH_3)_2$	Toluene; 25 °C for 1 h	Vacuum sublimn, 40 °C	Colorless crystalline solid, mp 92–95 °C
$Cl_2Al(CH_3)NC_2H_4N(CH_3)_3$	Toluene, 25 °C for 2 h	Vacuum sublimn, 100 °C	Yellow glassy solid, dec pt 145 °C, insol in hydrocarbons

$N(C_2H_5)C_2H_4N(CH_3)_2^5$ and dialkylaluminum acetylacetonates.⁶ However, the derivatives, diethylaluminum 2-methoxyethoxide⁷ and diethylaluminum 2-dimethylaminoethoxide⁸ which might have been expected to be chelated were observed as associated dimers. The increased stability



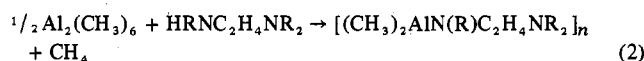
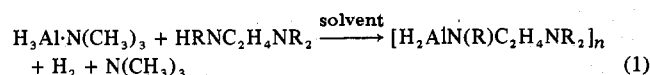
of chelated compounds makes it important to know what ligands to choose in order to synthesize monomeric chelated derivatives. To do this one must know what factors favor chelation over association and to what extent these factors apply to specific compounds.

In this paper we report the results of a study designed to elucidate the factors which favor chelation as they apply to organoaluminum-nitrogen compounds. Many new compounds have been synthesized and thoroughly characterized by cryoscopic molecular weight measurements and by variable-temperature and concentration-dependent ¹H NMR studies. The nature of the groups bound to aluminum and the chelating ligand bases, including potential ring size and relative ligand basicity, have been noted as affecting chelation.

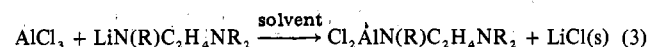
Experimental Section

All compounds described in this investigation were manipulated in a vacuum line or a purified nitrogen atmosphere. The solvents and reagents were purified by conventional means. Trimethylamine-alane ($H_3Al-N(CH_3)_3$) was prepared by the method of Ruff and Hawthorne.⁹ Triphenylalane was prepared by the method of Laubengayer, Wade, and Lengnick.¹⁰

Synthesis of Compounds. The compounds prepared for this study involved hydrido-, alkyl-, aryl-, and chloroaluminum derivatives. In the case of the hydrido and organo derivatives, the appropriate dibasic ligand was reacted with $H_3Al-N(CH_3)_3$ ⁹ or the organoalane⁵ according to previously reported procedures. The reactions are summarized by eq 1 and 2. In all cases, the extent of reaction, as measured by the



evolved H_2 , CH_4 , or C_2H_6 , was greater than 95% (frequently 99%) of that expected based on the balanced chemical equation. The chloroaluminum derivatives were prepared from $AlCl_3$ and the lithium salt of the dibasic ligand as shown by eq 3. The specific reaction



conditions, the methods of purification of product, and the physical properties of the products at room temperature are given in Table I.

Analysis. All compounds were analyzed for aluminum by EDTA titration,¹¹ for nitrogen by the standard Kjeldahl method, and for hydrolyzable aluminum-hydrogen, -methyl, or -ethyl content by measuring the evolved gas. In the case of chloroaluminum compounds, chlorine was determined by standard gravimetric procedures. The analytical data are summarized in Table II.

Infrared Spectra. The infrared spectra of all compounds were recorded in the range 4000–400 cm^{-1} by means of a Perkin-Elmer Model 457 spectrometer. The spectra were recorded as neat liquids or as Nujol and Kel-F mulls using KBr plates. Absorption intensities were measured using the method of Durkin, Glore, and DeHayes.¹² Following are the spectral data: frequency, cm^{-1} (intensity: s, strong; m, medium; w, weak; sh, shoulder). Bands due to the mulling agents have been omitted.

$H_2AlN(CH_3)C_2H_4N(CH_3)_2$ (Nujol mull): 2810 (s), 2730 (w), 1765–1755 (vs), 1355 (m), 1341 (m), 1285 (s), 1275 (m), 1255 (m), 1212 (w), 1175 (m), 1160 (m), 1152 (m), 1130 (m), 1102 (m), 1088 (m), 1054 (m), 1028 (s), 969 (s), 948 (m), 890–875 (s), 850 (vs), 778 (s), 725 (s), 697 (vs), 625 (s), 537 (s), 500 (sh, m), 445 (sh, m), 432 (m).

$H_2Al(C_2H_5)C_2H_4N(CH_3)_2$ (Nujol mull): 1767–1858 (vs), 1336 (m), 1304 (w), 1280 (m), 1266 (m), 1252 (w), 1197 (vs), 1175 (w), 1158 (m), 1147 (m), 1105 (m), 1078 (w), 1053 (m), 1028 (s), 996 (m), 955 (m), 900–880 (s), 825 (s), 788 (s), 760–755 (s), 695–685 (vs), 619 (s), 532 (s), 496 (m), 450 (m), 430 (m).

$(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$ (neat liquid): 3002 (m), 2950 (vs), 2915 (vs), 2880 (s), 2870 (sh, s), 2850 (m), 2800 (vs), 2780 (vs), 2730 (m), 2700 (m), 2670 (w), 2650 (w), 2575 (w), 1650 (vw), 1488 (sh, w), 1470 (s), 1462 (s), 1452 (sh, m), 1410 (w), 1394 (sh, w), 1387 (w), 1368 (m), 1344 (m), 1332 (s), 1307 (m), 1285 (m), 1245 (m), 1232 (m), 1208 (s), 1185–1178 (vs), 1147 (s), 1105 (w), 1059 (m), 1025 (m), 1015 (m), 950 (m), 883 (m), 850 (w), 785 (m), 710 (s), 660 (vs), 610 (m), 508–495 (w), 456 (w).

$(CH_3)_2AlN(CH_3)C_2H_4N(CH_3)_2$ (neat liquid): 2975 (vs), 2935 (vs),

Table II. Analytical Data

Compd	% Al		% N		% evolved gas		% Cl	
	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd
H ₂ Al(CH ₃)NC ₂ H ₅ N(CH ₃) ₂	20.74	21.15	21.52	22.68	1.55	1.39		
H ₂ Al(C ₂ H ₅)NC ₂ H ₄ N(CH ₃) ₂	18.72	19.00	19.43	18.90	1.40	1.34		
(CH ₃) ₂ Al(CH ₃)NC ₂ H ₄ N(CH ₃) ₂	17.07	17.83	17.71	17.90	19.00	18.92		
(CH ₃) ₂ Al(C ₂ H ₅)NC ₂ H ₄ N(CH ₃) ₂	15.68	16.20	16.27	16.11	17.47	17.51		
(CH ₃) ₂ Al(C ₂ H ₅)NC ₂ H ₄ N(C ₂ H ₅) ₂	13.48	13.44	14.02	14.02	15.02	14.83		
(CH ₃) ₂ Al(CH ₃)NC ₃ H ₆ N(CH ₃) ₂	15.68	14.98	16.27	16.31	17.47	17.51		
(C ₂ H ₅) ₂ Al(CH ₃)NC ₂ H ₄ N(CH ₃) ₂	14.49	14.39	15.04	14.96	31.20	30.76		
(C ₂ H ₅) ₂ Al(CH ₃)NC ₃ H ₆ N(CH ₃) ₂	13.48	14.03	14.02	12.33	29.03	29.25		
(CH ₃) ₂ AlSC ₂ H ₄ N(CH ₃) ₂	16.73	16.96			18.66	18.34		
(C ₂ H ₅) ₂ Al(C ₂ H ₅)NC ₂ H ₄ N(CH ₃) ₂	9.11	9.04	9.46	9.41				
Cl ₂ Al(C ₂ H ₅)NC ₂ H ₄ N(CH ₃) ₂	12.67	12.51	13.15	12.84			33.27	31.44
Cl ₂ Al(CH ₃)NC ₂ H ₄ N(CH ₃) ₂	13.56	13.87	14.06	13.17			35.56	37.57

2885 (s), 2860 (s), 2820 (vs), 2785 (sh, s), 2770 (vs), 2715 (m), 2670 (w), 1460 (s), 1407 (w), 1353 (w), 1344 (w), 1332 (w), 1313 (sh, w), 1288 (m), 1263 (m), 1233 (w), 1196 (vs), 1160 (m), 1150 (m), 1127 (w), 1099 (m), 1090–1080 (m), 1058 (sh, m), 1043 (s), 1032 (sh, m), 1010 (sh, m), 982 (w), 955 (sh, m), 943 (m), 915 (sh, m), 903 (m), 882 (m), 851 (m), 785 (m), 700–685 (vs), 670 (sh, vs), 630–620 (m), 573 (m), 515 (w), 495 (sh, w).

(CH₃)₂AlN(C₂H₅)C₂H₄N(C₂H₅)₂ (neat liquid): 2975 (vs), 2930 (vs), 2885 (vs), 2810 (vs), 2735 (m), 2650 (w), 2580 (w), 1472 (s), 1451 (m), 1405 (m), 1388 (s), 1370 (m), 1345 (m), 1337 (s), 1320 (sh, m), 1316 (m), 1300 (m), 1292 (sh, m), 1263 (m), 1227 (m), 1195 (vs), 1176 (sh, s), 1154 (sh, m), 1133 (m), 1105 (s), 1091 (s), 1073–1063 (s), 1054 (s), 1029 (m), 1009 (m), 970 (m), 943 (m), 923 (m), 913 (sh, w), 884 (m), 853 (m), 820 (m), 805 (sh, m), 790 (m), 772 (m), 746 (m), 695 (vs), 667 (vs), 608 (s), 562 (m), 508 (w), 448 (w).

(CH₃)₂AlN(CH₃)C₃H₆N(CH₃)₂ (neat liquid): 2970 (sh, vs), 2935 (vs), 2895 (vs), 2865 (vs), 2820 (vs), 2790 (vs), 2770 (vs), 2735 (m), 1473 (s), 1462 (s), 1448 (sh, m), 1435 (sh, m), 1389 (m), 1379 (m), 1327 (m), 1272 (m), 1250 (m), 1208–1200 (vs), 1156 (s), 1134 (m), 1103 (m), 1090 (m), 1065 (s), 1045 (s), 1017 (m), 973 (m), 918 (s), 869 (m), 845 (m), 830 (m), 715–675 (vs), 635 (sh, m), 620 (m), 575 (s), 518 (m).

(C₂H₅)₂AlN(CH₃)C₃H₆N(CH₃)₂ (neat liquid): 2980 (sh, s), 2945 (vs), 2908 (vs), 2870 (vs), 2815 (s), 2795 (m), 2775 (s), 2735 (m), 1475 (m), 1465 (m), 1415 (m), 1391 (m), 1380 (m), 1328 (w), 1273 (w), 1251 (w), 1237 (w), 1205 (m), 1157 (m), 1107 (m), 1090 (sh, m), 1070 (m), 1047 (m), 1016 (m), 987 (m), 960 (m), 912 (m), 870 (w), 846 (m), 831 (w), 660–640 (vs), 557 (m).

(C₂H₅)₂AlN(CH₃)C₂H₄N(CH₃)₂ (neat liquid): 3500–330 (w), 2980–2760 (vs), 2725 (s), 2675 (m), 1470–1460 (vs), 1412 (s), 1387 (m), 1373 (m), 1346 (s), 1335 (m), 1315 (m), 1290 (s), 1268 (s), 1236 (s), 1221 (s), 1185 (vs), 1160 (s), 1129 (m), 1100 (sh, s), 1093 (s), 1043 (vs), 1027 (vs), 1015 (s), 985 (vs), 899 (vs), 905 (vs), 884 (s), 855 (s), 786 (m), 670–595 (vs), 570–550 (sh, s), 495 (m), 463 (m), 437 (m).

(C₂H₅)₂AlN(C₂H₅)C₂H₄N(CH₃)₂ (Nujol mull, Kel-F mull): 3062 (m), 2963 (m), 2825 (w), 2785 (w), 1583 (w), 1467 (m), 1425 (m), 1389 (m), 1335 (s), 1291 (m), 1250 (m), 1235 (m), 1213 (m), 1175 (m), 1146 (m), 1130 (m), 1083 (s), 1062 (m), 1025 (m), 1015 (m), 1000 (m), 953 (m), 940 (m), 878 (m), 787 (m), 735 (s), 711 (vs), 678 (s), 593 (w), 580 (m), 511 (w), 475 (s), 465 (s), 455 (m), 435 (m), 419 (m).

(CH₃)₂AlOC₂H₄N(CH₃)₂ (Nujol mull, Kel-F mull): 3400–3060 (w), 3015 (w), 2990 (w), 2970 (w), 2960 (w), 2925 (m), 2885 (m), 1495 (w), 1470 (m), 1410 (m), 1387 (m), 1355 (w), 1350 (m), 1275 (m), 1260 (m), 1251 (m), 1192 (s), 1180 (sh, m), 1100 (s), 1077 (m), 1033 (m), 957 (m), 910 (s), 798 (m), 705 (br, s), 675 (br, vs), 570 (m), 530 (w), 449 (m), 405 (m).

(CH₃)₂AlSC₂H₄N(CH₃)₂ (Nujol mull, Kel-F mull): 3010 (w), 2980 (w), 2930 (m), 2890 (m), 2870 (m), 2820 (w), 1480 (m), 1468 (m), 1455 (m), 1435 (m), 1412 (m), 1387 (w), 1368 (m), 1303 (s), 1258 (w), 1245 (m), 1222 (m), 1193 (s), 1175 (m), 1119 (m), 1111 (sh, w), 1039 (m), 1025 (m), 997 (m), 948 (m), 898 (w), 775 (m), 712 (s), 672 (vs), 587 (s), 543 (w), 500 (m), 400 (s).

Cl₂AlN(C₂H₅)C₂H₄N(CH₃)₂ (Nujol mull): 1498 (m), 1421 (m), 1337 (vs), 1296 (s), 1272 (m), 1246 (s), 1222 (s), 1184 (vs), 1145 (vs), 1113 (m), 1063 (s), 1018 (sh, m), 1010 (s), 950 (s), 942 (sh, m), 895 (s), 785 (s), 725 (m), 660 (sh, w), 639 (vs), 595 (m), 537

(m), 497–492 (vs), 464 (s), 439 (s), 412 (s).

Cl₂AlN(CH₃)C₂H₄N(CH₃)₂ (Nujol mull): 3040 (m), 2825 (m), 1411 (m), 1349 (m), 1287 (m), 1275 (s), 1242 (m), 1205 (w), 1196 (w), 1150 (m), 1135 (m), 1111 (m), 1080 (m), 1055 (vs), 1013 (s), 1000 (s), 980 (vs), 942 (s), 855 (vs), 786 (m), 728 (w), 661 (vs), 550–530 (s), 492 (vs), 477 (vs).

Nuclear Magnetic Resonance Spectra. The ¹H NMR spectra of the compounds were recorded at 100 MHz using a JEOLCO MH-100 spectrometer equipped with variable-temperature capability. Unless otherwise stated, cyclopentane was used as solvent. All chemical shifts (Table III) are given in ppm and are referenced to tetramethylsilane as 0.00 ppm. Upfield shifts are denoted as plus values and downfield shifts as minus values. Variable-temperature and concentration-dependent data are given in the Results and Discussion.

Molecular Weight Measurements. Molecular weight measurements were obtained cryoscopically in benzene (+5 °C) as previously described.⁵ The data are given in Table IV. The calculated molality is based on the molecular weight of the monomer.

Results and Discussion

The ultimate goal of this research was the elucidation of the factors which favor the formation of a monomeric, chelated, four-coordinate organoaluminum–nitrogen species instead of an associated dimer. The detailed nature of a chelated, monomeric species and the corresponding associated dimer have been demonstrated by the chemical and spectroscopic properties⁵ of (CH₃)₂AlN(C₂H₅)C₂H₄N(CH₃)₂. This compound exists as a monomeric species in benzene solution but as an equilibrium mixture of monomer and dimer in cyclopentane solution. The dimer is favored at lowered temperatures. The structure of the monomeric species involves chelation of the nitrogen ligand to form a five-membered ring with a four-coordinate aluminum atom, whereas the dimer has a four-membered ring with bridging nitrogen atoms. Other structures including those with bridging methyl groups and mixed bridging atoms are inconsistent with available data. All of the compounds reported in this paper have properties which suggest structures similar to those of the previously discussed monomeric chelate and associated dimer.⁵ The degree of association of a given compound is determined by a variety of factors, with the most important ones being the substituents on the aluminum and nitrogen atoms. Molecular weight data, in conjunction with ¹H NMR spectroscopic data (including variable-temperature studies) and physical data have been used to distinguish those compounds which exist as chelated monomers, dimers, or equilibrium mixtures of the two. Table V lists the compounds according to these three general categories.

The new compound, (CH₃)₂AlN(CH₃)C₂H₄N(CH₃)₂, exists as an equilibrium mixture of the monomeric chelate and the associated dimer in both benzene and cyclohexane solution. However, this compound is more associated in the aliphatic solvents. This agrees with similar observations⁵ for the previously discussed (CH₃)₂AlN(C₂H₅)C₂H₄N(CH₃)₂. In the case of (CH₃)₂AlN(CH₃)C₂H₄N(CH₃)₂, the equilibrium

Table III. ¹H NMR Spectral Data^{a,b} (C₅H₁₀ Solution)

Compd	CH ₃ N	(CH ₃) ₂ N	(CH ₃)Al	Other
H(CH ₃)NC ₂ H ₄ N(CH ₃) ₂	-2.37	-2.15		-2.54 m (C ₂ H ₄)
H(C ₂ H ₅)NC ₂ H ₄ N(CH ₃) ₂		-2.15		-2.62 m (C ₂ H ₄)
				-1.03 t (CH ₃ CH ₂)
H(CH ₃)NC ₃ H ₆ N(CH ₃) ₂	-2.32	-2.10		-2.54 t (C ₃ H ₆)
				-2.24 m (C ₃ H ₆)
H(C ₂ H ₅)NC ₂ H ₄ N(C ₂ H ₅) ₂				-2.52 m, -1.01 q
HOC ₂ H ₄ N(CH ₃) ₂		-2.17		-4.53 s (OH)
				-3.50 t (C ₂ H ₄)
HSC ₂ H ₄ N(CH ₃) ₂		-2.17		-2.35 t (C ₂ H ₄)
(C ₂ H ₅) ₃ Al				-2.45 m (C ₂ H ₄)
				-1.11 t (CH ₃ CH ₂ Al)
				-0.38 q (CH ₃ CH ₂ Al)
H ₂ AlN(CH ₃)C ₂ H ₄ N(CH ₃) ₂	-2.35	-2.29		Al(H) ₂ and C ₂ H ₄
				not obsd
H ₂ AlN(C ₂ H ₅)C ₂ H ₄ N(CH ₃) ₂		-2.28		-2.92 m (C ₂ H ₄)
				-2.47 m (C ₂ H ₄)
(CH ₃) ₂ AlN(CH ₃)C ₂ H ₄ N(CH ₃) ₂	-2.44	-2.19	+0.78	-2.75 m (C ₂ H ₄)
(CH ₃) ₂ AlN(C ₂ H ₅)C ₂ H ₄ N(CH ₃) ₂		-2.37	+0.94	-2.88 m (C ₂ H ₄)
(CH ₃) ₂ AlN(C ₂ H ₅)C ₂ H ₄ N(C ₂ H ₅) ₂			+0.69	-2.83 m (C ₂ H ₄)
			+0.91	-2.48 m (C ₂ H ₄)
(CH ₃) ₂ AlN(CH ₃)C ₃ H ₆ N(CH ₃) ₂	-2.46	-2.16	+0.78	-2.75 m (C ₃ H ₆)
(C ₂ H ₅) ₂ AlN(CH ₃)C ₂ H ₄ N(CH ₃) ₂	-2.56	-2.24		-2.88 m (C ₂ H ₄)
				-1.07 t (CH ₃ CH ₂ Al)
				~0.00 q (CH ₃ CH ₂ Al)
(C ₂ H ₅)AlN(CH ₃)C ₃ H ₆ N(CH ₃) ₂	-2.43	-2.11		-2.68 m (C ₃ H ₆)
				-1.04 t (CH ₃ CH ₂ Al)
				0.00 q (CH ₃ CH ₂ Al)
(CH ₃) ₂ AlOC ₂ H ₄ N(CH ₃) ₂		-2.21	+1.02	-3.62 t (C ₂ H ₄)
				-2.47 t (C ₂ H ₄)
(CH ₃) ₂ AlSC ₂ H ₄ N(CH ₃) ₂		-2.48	+0.72	-2.77 m (C ₂ H ₄)

^a Shifts in ppm from TMS, + values, upfield; - values, downfield. ^b Key: s, singlet; t, triplet; q, quartet; m, multiplet.

Table IV. Molecular Weight of Aluminum Complexes in Benzene Solution

Compd	Calcd molality monomer	Deg of assoc
H ₂ AlN(CH ₃)C ₂ H ₄ N(CH ₃) ₂	0.135	2.11
	0.168	2.05
	0.182	2.01
H ₂ AlN(C ₂ H ₅)C ₂ H ₄ N(CH ₃) ₂	0.0884	1.97
	0.176	1.99
(CH ₃) ₂ AlN(CH ₃)C ₂ H ₄ N(CH ₃) ₂	0.0457	1.41
	0.135	1.55
	0.142	1.56
(CH ₃) ₂ AlN(C ₂ H ₅)C ₂ H ₄ N(CH ₃) ₂	0.0344	1.06
	0.0569	1.06
	0.0824	1.10
	0.103	1.10
(CH ₃) ₂ AlN(C ₂ H ₅)C ₂ H ₄ N(C ₂ H ₅) ₂	0.0765	1.09
	0.0949	1.11
(CH ₃) ₂ AlN(CH ₃)C ₃ H ₆ N(CH ₃) ₂	0.0535	1.75
	0.0950	1.84
(CH ₃) ₂ AlOC ₂ H ₄ N(CH ₃) ₂	0.0929	1.96
(CH ₃) ₂ AlSC ₂ H ₄ N(CH ₃) ₂	0.0887	1.12
	0.0926	1.14
(C ₂ H ₅) ₂ AlN(CH ₃)C ₂ H ₄ N(CH ₃) ₂	0.0882	1.20
(C ₂ H ₅) ₂ AlN(CH ₃)C ₃ H ₆ N(CH ₃) ₂	0.0490	1.67
	0.100	1.75
(C ₆ H ₅) ₂ AlN(C ₂ H ₅)C ₂ H ₄ N(CH ₃) ₂	0.0620	1.10
	0.0713	1.05
Cl ₂ AlN(C ₂ H ₅)C ₂ H ₄ N(CH ₃) ₂	0.0347	1.22
	0.0747	1.18
	0.0908	1.13

constants for the monomer to dimer equilibrium, calculated from cryoscopic molecular weight data, average 33 for benzene and 57 for cyclohexane solutions. The ¹H NMR spectrum of this compound, neat and in cyclopentane and benzene solution, is temperature dependent. The temperature range of +140 to -60 °C was studied. As the temperature was lowered, the Al(CH₃)₂ line moved to lower field, broadened, and finally separated into two distinct lines of equal intensity. For a cyclopentane solution these two low-temperature

Table V. Nature of Compounds

Monomeric chelated derivative	Dimeric species	Equilibrium mixture
(CH ₃) ₂ AlN(C ₂ H ₅)C ₂ H ₄ N(CH ₃) ₂	H ₂ AlN(CH ₃)C ₂ H ₄ N(CH ₃) ₂	(CH ₃) ₂ AlN(CH ₃)C ₂ H ₄ N(CH ₃) ₂
(CH ₃) ₂ AlN(C ₂ H ₅)C ₂ H ₄ N(C ₂ H ₅) ₂	H ₂ AlN(C ₂ H ₅)C ₂ H ₄ N(CH ₃) ₂	(CH ₃) ₂ AlN(CH ₃)C ₂ H ₄ N(CH ₃) ₂
(CH ₃) ₂ AlSC ₂ H ₄ N(CH ₃) ₂	(CH ₃) ₂ AlOC ₂ H ₄ N(CH ₃) ₂	(C ₂ H ₅) ₂ AlN(CH ₃)C ₂ H ₄ N(CH ₃) ₂
(C ₆ H ₅) ₂ AlN(C ₂ H ₅)C ₂ H ₄ N(CH ₃) ₂	(C ₂ H ₅) ₂ AlN(CH ₃)C ₂ H ₄ N(CH ₃) ₂	(C ₂ H ₅) ₂ AlN(CH ₃)C ₂ H ₄ N(CH ₃) ₂
Cl ₂ AlN(C ₂ H ₅)C ₂ H ₄ N(CH ₃) ₂		C ₃ H ₆ N(CH ₃) ₂

Al(CH₃)₂ lines were observed at +0.75 and +0.81 ppm at -35 °C. Cooling to -50 °C was required for splitting in a toluene-*d*₈ solution. Further cooling produced no further change in the spectrum. The intensities of these two Al(CH₃)₂ lines were not dependent upon concentration. The N(CH₃)₂ line moved to higher field upon cooling but finally at the very low temperature (-60 °C) was at lower field (-2.23 ppm) than at 30 °C (-2.19 ppm). The N(CH₃) line was not affected by lowering the temperature.

The temperature dependence of the ¹H NMR spectrum of (CH₃)₂AlN(CH₃)C₂H₄N(CH₃)₂ can be related to a rapid equilibrium between the chelated monomer and the dimer which is shifted toward the dimer with decreasing temperature. However, at and below the temperature at which splitting occurs, only the dimeric species is present in sufficient concentration to be observed. The relatively large equilibrium constant and observations in both cyclopentane and toluene solutions support this conclusion. Furthermore, it must be remembered that the dimer has twice as many observable protons per molecule as the chelated monomer. The dimer molecule must be in a cis conformation relative to the nitrogen-bridged four-membered ring (Figure 1) to account for the two equal Al-CH₃ lines at low temperature. The cis isomer has two nonequivalent Al-CH₃ groups, giving two

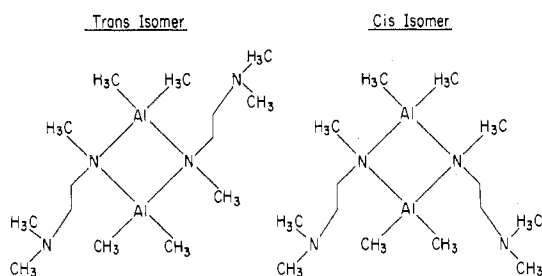


Figure 1. Geometric isomers of the $(\text{CH}_3)_2\text{Al}(\text{CH}_3)\text{NC}_2\text{H}_4\text{N}(\text{CH}_3)_2$ dimer.

Al-CH₃ lines, and one N-CH₃ group bound to the bridging nitrogen. The trans isomer has only one type of Al-CH₃ and one type of bridging N-CH₃. It is unlikely that a mixture of both cis and trans isomers would give rise to two equal Al-CH₃ lines whose relative intensities are independent of both concentration and temperature. An additional explanation for the temperature dependence of the spectrum could involve a bent and inverting four-membered aluminum-nitrogen ring. At room temperature a rapidly inverting four-membered ring, interconverting axial and equatorial Al-CH₃ groups, would also lead to one NMR line. However, the changes in chemical shifts with temperature and the molecular weight data suggest the presence of at least a small concentration of the monomeric chelate. A remaining question concerns the preference of the dimer for the cis configuration. This is believed to be related to the mode of dimer formation. If molecular models are used, it can be seen that there is significantly less steric hindrance for bringing two chelated monomers together to form a cis dimer than a trans dimer. Once the four-membered ring of the dimer has been formed and the chelate rings opened, the two isomers have similar steric requirements. There is also some evidence that the N(CH₃)₂ groups might be interacting weakly with aluminum atoms of the dimer to form five-coordinate aluminum. The chemical shift of the N(CH₃)₂ group moves to lower field upon cooling from +30 to -60 °C. The bound N(CH₃)₂ group in the chelated monomer is observed at lower field than the free ligand or in the dimer of $(\text{C}_2\text{H}_5)_2\text{AlN}(\text{C}_2\text{H}_5)_2\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2$.⁵ A stronger interaction of an N(CH₃)₂ group is suggested to occur in the less sterically hindered $[\text{H}_2\text{AlN}(\text{CH}_3)_2\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2]_2$.

Definite evidence for both cis and trans isomers is provided by data for the compound $(\text{CH}_3)_2\text{AlN}(\text{CH}_3)\text{C}_3\text{H}_6\text{N}(\text{CH}_3)_2$. This derivative is more associated than the previously discussed compound, $(\text{CH}_3)_2\text{AlN}(\text{CH}_3)\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2$. The temperature dependence of the ¹H NMR spectrum is also different. When a sample in C₅H₁₀ was cooled from 30 °C, the Al(CH₃)₂ line broadened and finally resolved into three closely spaced lines at +0.75, +0.78, and +0.81 ppm at -35 °C, the same temperature at which splitting occurred for $(\text{CH}_3)_2\text{AlN}(\text{CH}_3)\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2$. The N-CH₃ group exhibited two lines of unequal intensity at -2.42 and -2.36 ppm. The lower field line was the more intense. The N(CH₃)₂ line did not change with temperature. These data suggest the presence of both cis and trans isomers for the dimer, in contrast to the single isomer observed for $(\text{CH}_3)_2\text{AlN}(\text{CH}_3)\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2$. The four-membered aluminum-nitrogen ring might also be bent and rapidly inverting at room temperature. A comparison of the chemical shift data for $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2]_2$ and $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)\text{C}_3\text{H}_6\text{N}(\text{CH}_3)_2]_2$ suggests that the cis isomer is significantly more abundant than the trans isomer. Another possible or additional interpretation for the temperature dependence of the NMR spectrum is an isomerization process in which one aluminum-nitrogen bond of the dimer breaks. Then, if there is rotation about one other aluminum-nitrogen bond, isomerization to form both isomers could occur without the formation of the chelate.

Another compound whose NMR spectrum is of interest is $\text{H}_2\text{AlN}(\text{CH}_3)_2\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2$. This compound is dimeric in benzene solution. The apparent molecular weight does not depend on concentration. The NMR spectrum of a C₅H₁₀ solution at room temperature has one NCH₃ line (-2.53 ppm) and one N(CH₃)₂ line (-2.29 ppm). The AlH₂ line was not observed, probably due to quadrupole broadening. Upon lowering the temperature, the N(CH₃)₂ line broadened and finally resolved at -35 °C into two lines of similar intensity (-2.33 and -2.20 ppm). As the temperature was lowered further to -49 °C, the low-field line increased in intensity slightly. Observation of solutions of various concentrations suggested that the spectrum did not depend upon concentration. However, the temperature and concentration dependence of the spectrum could not be firmly established by integration due to the presence of overlapping solvent sidebands. There was no change in the spectrum of a toluene-*d*₈ solution with decreasing temperature (-70 °C). An on-off equilibrium of the N(CH₃)₂ groups of the dimer, which would involve a five-coordinate aluminum atom, could account for the observed temperature dependence of the C₅H₁₀ solutions. The two NMR lines for the N(CH₃)₂ group would correspond to the bound and unbound configurations. The aluminum-hydrogen compounds $\text{H}_3\text{Al}[\text{N}(\text{CH}_3)_2\text{CH}_2\text{N}(\text{CH}_3)_2]_2$ ¹⁵ and the dimer and trimer of $\text{H}(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_3$ ¹⁶ are several examples of five-coordinate aluminum. The low-field, low-temperature line (-2.33 ppm) is assigned to the bound N(CH₃)₂ group since its chemical shift is close to that observed for the bound N(CH₃)₂ group in the monomeric chelate of $(\text{CH}_3)_2\text{AlN}(\text{C}_2\text{H}_5)_2\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2$ (-2.37 ppm). The high-field line (-2.20 ppm) must then be assigned to the free N(CH₃)₂ group as its shift is close to that of the free ligand (-2.15 ppm). Probably only one isomer of the dimer is present as only one bridging NCH₃ line is observed. If both isomers were present, more than one line would be expected, as observed for $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)\text{C}_3\text{H}_6\text{N}(\text{CH}_3)_2]_2$. The cis isomer might be expected based on its predominance in the other compound discussed. However, the steric hindrance for five-coordinate aluminum might be less for a trans species.

The infrared spectrum of $[\text{H}_2\text{AlN}(\text{CH}_3)_2\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2]_2$ is also consistent with a five-coordinate aluminum atom. There is a band at 1760 cm⁻¹ with a shoulder at 1700 cm⁻¹. Previous workers^{13,14} have attempted to correlate the Al-H stretching frequency with the coordination number of aluminum. Lower frequencies (1700-1720 cm⁻¹) are generally observed for five-coordinate aluminum complexes, while higher frequencies (1750-1800 cm⁻¹) are noted for four-coordinate species.

Another dimeric product is $[(\text{CH}_3)_2\text{AlOC}_2\text{H}_4(\text{CH}_3)_2]_2$. This compound is similar to $[(\text{C}_2\text{H}_5)_2\text{AlOC}_2\text{H}_4\text{N}(\text{CH}_3)_2]_2$.⁸ The structure probably involves a four-membered aluminum-oxygen ring with the N(CH₃)₂ groups being unbound. The chemical shift of the N(CH₃)₂ group protons is -2.21 ppm, very close to the shift in the free ligand (-2.19 ppm). The Al(CH₃)₂ line is a singlet at +1.02 ppm. No low-temperature spectra were recorded. In contrast to $[(\text{CH}_3)_2\text{AlOC}_2\text{H}_4\text{N}(\text{CH}_3)_2]_2$, the compound $(\text{CH}_3)_2\text{AlSC}_2\text{H}_4\text{N}(\text{CH}_3)_2$ is a monomeric chelate. At room temperature it exists as a crystalline solid and melts sharply at 65-67 °C. This, together with a sublimation temperature of 50 °C, suggests that the compound may also be a monomeric chelate in the solid state. The NMR spectrum has a line at -2.48 ppm for the N(CH₃)₂ group and one at +0.72 ppm for the Al(CH₃)₂ protons. The large difference in chemical shift for the N(CH₃)₂ group in the complex (-2.48 ppm) compared to the free ligand (-2.17 ppm) supports the premise that the N(CH₃)₂ group is bound to the aluminum. The relatively low-field chemical shift for the Al(CH₃)₂ protons might reflect the weaker donating power of sulfur as compared to that of oxygen and nitrogen. The

compounds $\text{Cl}_2\text{AlN}(\text{C}_2\text{H}_5)\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2$ and $(\text{C}_6\text{H}_5)_2\text{AlN}(\text{C}_2\text{H}_5)\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2$ are also essentially monomeric in benzene. They also have a relatively low sublimation temperature (50 and 90 °C, respectively) and, hence, are probably monomeric in the solid state as well.

Factors Affecting Chelation. Several factors such as steric effects, electronic effects, thermodynamic effects, and the mechanism of formation influence the degree of association of aluminum–nitrogen derivatives. Other factors such as chelate ring size, entropy, and base strengths should also affect chelate formation and stability. Several of these combined factors have been investigated in this study. Steric effects, the interplay between enthalpy and entropy, the relative base strengths of the two ligand base sites, chelate ring size, and, possibly, the mechanism of formation have been shown to play important roles in chelate formation. Our understanding of these factors and their effects on chelation and association should enable future workers to prepare other chelates.

Steric factors play the most important role in determining whether the monomeric chelate or the dimer is observed (Table V). It is apparent that the nature of both the groups bound to the aluminum and the bridging nitrogen are significant. For example, when methyl groups are bound to aluminum, it is necessary to have an ethyl group on the bridging nitrogen to have a monomeric chelate. If hydrogens are bound to aluminum, an $\text{N}-\text{C}_2\text{H}_5$ bridging group is insufficient to lead to the chelate. A dimer is observed instead. Furthermore, if ethyl groups are bound to aluminum, a methyl group on the bridging nitrogen does not produce sufficient steric hindrance to prevent the dimer from forming. Thus, the steric effects of the group bound to the bridging nitrogen might be more important than those on aluminum. By considering molecular weight data for other compounds in Table IV, it can be seen that the steric effect of the groups on the chelating nitrogen, the $-\text{NR}_2$ groups, is relatively unimportant.

The chelate ring size also has an effect on the stability of the chelated monomer. As the ring size increases from a five- to a six-membered ring, the chelate becomes less stable. This effect may be related to the increased entropy for the unbound longer chains in the dimers over those with shorter chains, resulting in a smaller decrease in entropy when dimers are formed.

The relative base strengths of the two bases of the chelating ligand also can have a significant role. In general, the base strengths of Lewis bases are affected by the steric and electronic properties of groups bound to the basic atom. The compound $(\text{CH}_3)_2\text{AlSC}_2\text{H}_4\text{N}(\text{CH}_3)_2$ is a monomeric chelate.

The $-\text{N}(\text{CH}_3)_2$ group is apparently a stronger base than the bridging sulfur. Hence, chelation is observed. In the case of $(\text{CH}_3)_2\text{AlOC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, chelation might also be expected as amines are usually stronger bases than ethers.¹⁷ However, only a dimer is observed. The polarization of the aluminum–oxygen bond due to the difference in electronegativity could account for the increased basicity of the bridging oxygen.⁷ In addition, the steric effects of the methyl groups would help to decrease the basicity of the $-\text{N}(\text{CH}_3)_2$ group.¹⁵

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Registry No. $\text{H}_2\text{Al}(\text{CH}_3)\text{NC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, 59738-49-7; $\text{H}_2\text{-Al}(\text{C}_2\text{H}_5)\text{NC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, 59738-50-0; $(\text{CH}_3)_2\text{Al}(\text{CH}_3)\text{NC}_2\text{H}_4\text{-N}(\text{CH}_3)_2$, 59738-37-3; $(\text{CH}_3)_2\text{Al}(\text{C}_2\text{H}_5)\text{NC}_2\text{H}_4\text{N}(\text{C}_2\text{H}_5)_2$, 59738-38-4; $(\text{CH}_3)_2\text{Al}(\text{CH}_3)\text{NC}_3\text{H}_6\text{N}(\text{CH}_3)_2$, 59738-39-5; $(\text{C}_2\text{H}_5)_2\text{-Al}(\text{CH}_3)\text{NC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, 59738-40-8; $(\text{C}_2\text{H}_5)_2\text{Al}(\text{CH}_3)\text{NC}_3\text{H}_6\text{-N}(\text{CH}_3)_2$, 59738-41-9; $(\text{CH}_3)_2\text{AlOC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, 59738-42-0; $(\text{CH}_3)_2\text{AlSC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, 59738-43-1; $(\text{C}_6\text{H}_5)_2\text{Al}(\text{C}_2\text{H}_5)\text{NC}_2\text{H}_4\text{-N}(\text{CH}_3)_2$, 59738-44-2; $\text{Cl}_2\text{Al}(\text{C}_2\text{H}_5)\text{NC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, 59738-07-7; $\text{Cl}_2\text{Al}(\text{CH}_3)\text{NC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, 59738-08-8; $(\text{CH}_3)_2\text{Al}(\text{C}_2\text{H}_5)\text{NC}_2\text{-H}_4\text{N}(\text{CH}_3)_2$, 55975-87-6; $\text{H}(\text{CH}_3)\text{NC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, 142-25-6; $\text{H}(\text{C}_2\text{H}_5)\text{NC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, 123-83-1; $\text{H}(\text{CH}_3)\text{NC}_3\text{H}_6\text{N}(\text{CH}_3)_2$, 4543-96-8; $\text{H}(\text{C}_2\text{H}_5)\text{NC}_2\text{H}_4\text{N}(\text{C}_2\text{H}_5)_2$, 105-04-4; $\text{HOC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, 24721-92-4; $\text{HSC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, 108-02-1; $(\text{C}_2\text{H}_5)_3\text{Al}$, 97-93-8; $\text{H}_3\text{Al-N}(\text{CH}_3)_3$, 17013-07-9; triphenylalane, 841-76-9; Al_2Me_6 , 15632-54-9.

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Dithiocarbamates of Cu(I), Cu(II), and Cu(III). An Electrochemical Study

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An electrochemical study of the $\text{Cu}^{n+}/[\text{R}_2\text{dtc}]^-$ system in aprotic solvents defines the electron transfer relationships between bis-chelated complexes of copper in the three oxidation states I, II, and III. $\text{Cu}(\text{R}_2\text{dtc})_2$ undergoes single one-electron oxidation and reduction steps at a platinum electrode: $[\text{Cu}^{\text{III}}(\text{R}_2\text{dtc})_2]^+ + e^- = \text{Cu}^{\text{II}}(\text{R}_2\text{dtc})_2$; $\text{Cu}^{\text{II}}(\text{R}_2\text{dtc})_2 + e^- = [\text{Cu}^{\text{I}}(\text{R}_2\text{dtc})_2]^-$. These redox processes have been characterized for 16 different substituents R by normal pulse voltammetry, ac voltammetry, cyclic voltammetry, spectroelectrolysis, and coulometry. Bis-chelated Cu(I) complexes have been characterized in solution although attempts to isolate the $[\text{Cu}(\text{R}_2\text{dtc})_2]^-$ anion in the solid state failed. The redox potentials vary strongly with the nature of the substituent.

Introduction

During the past decade, it has been established that the dithiocarbamate ligand (I) confers on transition metals many

unusual properties such as spin isomerism of the iron(III) complexes¹ and the oligomeric structures of the silver(I) (hexameric),² copper(I) (tetrameric),³ and gold(I) (dimeric)⁴