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# Reactions of Transition-Metal–Nitrogen σ Bonds. 5.[1] Carbonation of Tetrakis(diethylamido)chromium(IV) To Yield Binuclear Chromium(III) and -(II) Carbamato Complexes

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From the reaction between $Cr(NEt_2)_4$ and $CO_2$ (4 equiv) two crystalline compounds have been isolated and structurally characterized: I, $Cr_2(O_2CNEt_2)_4(\mu\text{-}NEt_2)_2$; II, $Cr_2(O_2CNEt_2)_4{\cdot}2HNEt_2$. Compound I is the major product when $CO_2$ is allowed to react slowly with $Cr(NEt_2)_4$; compound II predominates when $CO_2$ (4 equiv) is added rapidly. These results are compared with previous studies of $CO_2$ insertion reactions involving early transition-metal dialkylamides and with the known reactions of $Cr(NEt_2)_4$. A reaction pathway leading from $Cr(NEt_2)_4$ to I and II is proposed to involve β-hydrogen elimination from a $[Cr^{IV}–NEt_2]$ moiety followed by reductive elimination of $Et_2NH$ and the generation of Cr(II). I crystallizes in space group *Pbcn* with $a = 19.122$ (8) Å, $b = 11.024$ (2) Å, $c = 18.114$ (6) Å, $V = 3818$ (3) Å$^3$, and $Z = 4$. The structure was solved and refined to yield $R_1 = 0.082$ and $R_2 = 0.109$. I has crystallographic $C_2$ symmetry and consists of two distorted edge-sharing octahedra with bridging diethylamido groups. The $Cr_2N_2(O–O)_4$ moiety has virtual $D_2$ symmetry. Important distances are Cr–Cr = 2.948 (2) Å and Cr–N (average) = 2.046 Å; average Cr–O distances trans to N are 2.065 Å while Cr–O distances cis to N are 1.996 Å. II crystallizes in the space group $P\bar{1}$ with $a = 10.936$ (2) Å, $b = 11.170$ (2) Å, $c = 8.871$ (2) Å, $\alpha = 99.46$ (1)°, $\beta = 98.56$ (1)°, $\gamma = 108.58$ (1)°, $V = 989.4$ (6) Å$^3$, and $Z = 1$. The structure was solved and refined to yield $R_1 = 0.071$ and $R_2 = 0.098$. The molecule adopts the classical dichromium tetracarboxylato-type structure with axial (Cr–Cr–N = 178.1 (3)°) diethylamine ligands. II has imposed $C_i$ symmetry with the $Cr_2O_8N_2$ core having nearly $D_{4h}$ symmetry; Cr–Cr = 2.384 (2) Å, Cr–N = 2.452 (8) Å, and Cr–O (average) = 2.018 (7) Å.

## Introduction

It is characteristic of early transition-metal dialkylamides, $M_m(NR_2)_n$, that they react readily in solution with carbon dioxide to yield complexes containing the carbamato anion $R_2NCO_2^-$ as a ligand.[1] In some cases, mononuclear dialkylamides react to convert all $R_2N$ groups to $R_2NCO_2$, as in (I), while for $W(NMe_2)_6$ only $W(NMe_2)_3(O_2CNMe_2)_3$ can

$$M(NMe_2)_n + nCO_2 \rightarrow M(O_2CNMe_2)_n \qquad (I)$$
$$M = Ti, V, Zr;\ n = 4$$
$$M = Nb, Ta;\ n = 5$$

be obtained even in the presence of excess $CO_2$. However, even in cases where fully carbonated products are obtainable, the use of $<n$ equiv of $CO_2$ allows the isolation of partly carbonated compounds such as $Ti(NMe_2)_2(O_2CNMe_2)_2$, $Ti(NMe_2)(O_2CNMe_2)_3$, and $Ta(NMe_2)_2(O_2CNMe_2)_3$.[1,3]

Similarly, several dinuclear, triply bonded dialkylamides react readily with $CO_2$. $W_2(NMe_2)_6$ and $W_2(NEt_2)_4Me_2$ have yielded, respectively, $W_2(O_2CNMe_2)_6$ and $W_2(O_2CNEt_2)_4Me_2$.[4]

All of these, and other, carbonation reactions have proceeded rapidly and essentially quantitatively without any observed changes in oxidation numbers, of the sort found when $CS_2$ is inserted, e.g.[5,6]

$$W(NMe_2)_6 + 6CS_2 \rightarrow W(S_2CNMe_2)_4 + (Me_2NC(S)S)_2$$

$$Nb(NMe_2)_5 + 5CS_2 \rightarrow Nb(S_2CNMe_2)_4 + {}^1/_2(Me_2NC(S)S)_2$$

Also, there has been no prior example of the conversion of a mononuclear metal dialkylamide to a binuclear carbamato product.

We report here the occurrence of an unprecedented type of reaction, in which both of the aforementioned processes take place when $Cr(NEt_2)_4$ reacts with an excess of $CO_2$. The reaction is complex and yields products in proportions depending sensitively upon reaction conditions. One compound which has *not* been detected is the "obvious" product, $Cr(O_2CNEt_2)_4$. We also show conclusively, by X-ray crystallography, the identity and structures of two of the products: $Cr_2(O_2CNEt_2)_4(\mu\text{-}NEt_2)_2$, I, a binuclear chromium(III) complex, and $Cr_2(O_2CNEt_2)_4{\cdot}2HNEt_2$, II, a quadruply bonded dichromium(II) complex in which bridging carbamato groups are observed for the first time in any quadruply bonded $M_2$ compound.

## Experimental Section

General procedures and physical instrumentation were as previously described.[1] $Cr(NEt_2)_4$ was prepared by a modification of the published procedure.[7] A diethyl ether/hexane solvent mixture was used for the reaction between $CrCl_3$ and $LiNEt_2$ (3 equiv).

**(1) Preparation of Bis(diethylamido)tetrakis(diethylcarbamato)dichromium(III).** $Cr(NEt_2)_4$ (5.78 mmol) in hexanes (180 mL) was exposed to $CO_2$ (25 mmol) in a calibrated vacuum manifold at room temperature. An immediate uptake of $CO_2$ was noted by a reduction in $CO_2$ pressure. After 10 min the remaining $CO_2$ was condensed into the reaction flask at −196 °C. The reaction mixture was then allowed to warm to room temperature and was stirred magnetically for 10 h. A fine pale blue-green precipitate was removed by filtration and the filtrate, which appeared dark green under fluorescent lighting and red in incandescent light, was reduced in volume to 120 mL and cooled −20 °C for 10 h yielding dark green crystals of $Cr_2(O_2CNEt_2)_4(\mu\text{-}NEt_2)_2$ which were collected and dried under vacuum (25 °C, $10^{-2}$ Torr); 0.738 g (36% yield based on Cr). Anal. Calcd for $C_{28}H_{60}N_6O_8Cr_2$: C, 47.18; H, 8.45; N, 11.79. Found: C, 46.77; H, 7.99; N, 11.02.

IR data obtained from a Nujol mull between CsI plates in the region 1500–200 cm$^{-1}$: 1485 (s), 1378 (s), 1337 (m), 1322 (s), 1262 (w), 1209 (m), 1133 (w), 1112 (m), 1099 (m), 1090 (m), 1083 (m), 1075 (m), 1040 (w), 1007 (w), 977 (w), 37 (w), 896 (w), 836 (s), 790 (s, br), 641 (s, br), 610 (s), 572 (w), 495 (s), 482 (m), 461 (m), 495 (s), 482 (m), 460 (m), 421 (m), 402 (m), 348 (m, br), 263 (w).

Mass spectral data obtained by direct insertion at 100 °C: *m/e* 712, $[Cr_2(O_2CNEt_2)_4(NEt_2)_2]^+$, small; *m/e* 641, $[Cr_2(O_2CNEt_2)_4(HNEt_2)]^+$, medium; *m/e* 640, $[Cr_2(O_2CNEt_2)_4NEt_2]^+$, base peak; *m/e* 596, $[Cr_2(O_2CNEt_2)_3(NEt_2)_2]^+$, small; *m/e* 563, large; *m/e* 452, $[Cr_2(O_2CNEt_2)_2(NEt_2)(HNEt)]^+$, medium; *m/e* 356, $[Cr(O_2CNEt_2)_2NEt_2]^+$, large. Magnetic susceptibility data obtained from toluene solution by the method of Evans[15] [$\mu_{eff}$ per Cr atom in $\mu_B$ (temperature in K)]: 2.25 (355); 2.15 (310); 2.09 (283); 2.00 (251); 1.86 (218); 1.78 (210).

**Reaction of $Cr_2(O_2CNEt_2)_4(NEt_2)_2$ with Excess $CO_2$.** $CO_2$ (3 mmol) was added to a frozen solution of $Cr_2(O_2CNEt_2)_4(NEt_2)_2$ (0.205 mmol) in toluene (10 mL) at −196 °C. The flask was warmed to room temperature and the solution was stirred for 13 h. The solvent was stripped, yielding a dark green solid which was identified as the starting material by IR spectroscopy.

**(2) Preparation of Bis(diethylamine)tetrakis(diethylcarbamato)dichromium(II).** $CO_2$ (15.33 mmol) was added to a frozen solution

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(−196 °C) of $Cr(NEt_2)_4$ (3.41 mmol) in hexane (50 mL). The closed system was allowed to warm to room temperature and stirred magnetically for 10 h. The resulting red solution contained a small amount of a pale blue-green precipitate which was removed by filtration. The filtrate was stripped to dryness, the residue was redissolved in hexane at ca. 60 °C, and the solution was cooled to ca. −20 °C yielding reddish orange crystals of $Cr_2(O_2CNEt_2)_4 \cdot 2HNEt_2$. Anal. Calcd for $C_{28}H_{62}N_6O_8Cr_2$: C, 47.04; H, 8.74; N, 11.70. Found: C, 47.0; H, 8.66; N, 11.61.

IR data obtained from a Nujol mull between CsI plates (1500–200 $cm^{-1}$): 1346 (s), 1330 (m), 1310 (w), 1271 (m), 1242 (w), 1188 (s), 1145 (s), 1085 (m), 1067 (s), 1047 (s), 996 (vs, br), 914 (m), 887 (m), 869 (vs), 788 (vs, br), 596 (s), 589 (s), 537 (s), 509 (m), 348 (vs), 328 (m), 316 (m), 297 (m), 230 (w). $^1H$ NMR (benzene-$d_6$, 30 °C): $\delta$ 2.10–5.90 (br, $CH_2$), 1.33 (t, $J$ = 6 Hz, $CH_3$); the compound is apparently slightly paramagnetic.

**Organic Volatiles Formed in the Reaction between $Cr(NEt_2)_4$ and $CO_2$.** A 50 mL round-bottomed flask containing neat $Cr(NEt_2)_4$ (3.47 mmol) was rotated to coat its walls with the dark green liquid. The flask was then attached to a vacuum manifold and, by cooling to −196 °C, $CO_2$ (10.4 mmol) was added. The system was allowed to warm to room temperature, and with the use of a heat gun all the volatiles were collected in an NMR tube containing toluene-$d_8$ frozen at −196 °C. The tube was then sealed with a torch. $^1H$ NMR spectroscopy revealed the presence of diethylamine and *N*-(ethylidene)ethylamine in approximately equal quantities. The $^1H$ NMR data obtained at 30 °C from toluene-$d_8$ at 60 MHz for $CH_3CH_2N{=}CHCH_3$ were $\delta$ 7.40 (m, br, $=CH$), 3.25 (q, $J$ = 7.9, $CH_2$), 1.70 (dt, $J$ = 4.9, $J_2$ = 1.1, $\mathit{CH}_3CH{=}NCH_2$), and 1.12 (t, $J$ = 7.0, $\mathit{CH}_3CH_2N$) which may be compared to the reported $^1H$ NMR data of $CH_3CH{=}NCH_3$: $\delta$ 7.67 (qq, $J_1$ = 4.8, $J_2$ = 1.8 $N{=}CH–$), 3.23 (dq, $J_1$ = 1.8, $J_2$ = 1.4, $CH_3N$), 1.92 (dq, $J_1$ = 4.8, $J_2$ = 1.4 $N{=}CH\mathit{CH}_3$). $\delta$ are in ppm relative to $Me_4Si$ and $J$ values are in Hz.

**Crystallographic Study of I.**[8] Crystals were mounted by wedging them in mineral oil filled, thin-walled capillaries, and several were examined before one of good quality was found, measuring 0.20 × 0.25 × 0.35 mm. $\omega$ scans of several intense reflections had peak widths at half-height of ca. 0.2°. Preliminary lattice constants and axial photographs indicated that the crystal belonged to the orthorhombic system. The final lattice constants, determined at 3 °C from the setting angles of 15 reflections in the range 23° < $2\theta$(Cu K$\alpha$) < 38°, chosen to give a good sampling of diffractometer settings and indices, are $a$ = 19.122 (8) Å, $b$ = 11.024 (2) Å, $c$ = 18.114 (6) Å, and $V$ = 3818 (2) Å$^3$. The observed volume was consistent with that expected for $Z$ = 4. The systematic absences observed during data collection, $0kl$ ($k = 2n + 1$), $h0l$ ($l = 2n + 1$), and $hk0$ ($h + k = 2n + 1$), uniquely determined the space group to be *Pbcn* (No. 60).

The data were collected using Cu K$\alpha$ (λ 1.541 84 Å) radiation at 3 °C with a Syntex $P\bar{1}$ autodiffractometer (located in a cold room maintained at 3 ± 1 °C) equipped with a graphite crystal monochromator. Variable scan rates from 4.0 to 24.0°/min were used for symmetric $\theta/2\theta$ scans ranging from 1.0° below to 1.0° above the calculated Cu K$\alpha_1$–K$\alpha_2$ doublet. A total of 3157 unique reflections having 0° < $2\theta$ (Cu K$\alpha$) < 120° were recorded. The ratio of background to scan time was 0.5. The intensities of three standard reflections were monitored frequently throughout data collection and showed no decrease in intensity. The data were reduced to a set of relative $|F_o|^2$ values. The intensities were corrected for absorption effects ($\mu$ = 53.3 $cm^{-1}$); transmission coefficients ranged from 0.325 to 0.433 with an average of 0.386. The 1512 reflections having $|F_o|^2 > 3\sigma(|F_o|^2)$ were retained as observed and used in subsequent structure solution and refinement. The positions of the 22 unique nonhydrogen atoms were determined using standard heavy-atom methods, i.e., a Patterson solution, followed by several rounds of least-squares refinement, and difference Fourier syntheses. Positional and isotropic thermal parameters of the 25 nonhydrogen atoms were refined in several least-squares cycles to yield discrepancy indices

$$R_1 = \sum||F_o| - |F_c||/|F_o| = 0.087$$

$$R_2 = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2} = 0.114$$

The structure was refined to convergence using anisotropic thermal parameters for the Cr, O, and N atoms and isotropic thermal parameters for the C atoms. The final discrepancy indices were $R_1$ = 0.082 and $R_2$ = 0.109. The estimated standard deviation of an observation of unit weight was 2.11. A final difference Fourier map showed no features of structural significance.

**Crystallographic Study of II.**[8] A crystal measuring ca. 0.25 × 0.4 × 0.4 mm was mounted, embedded in epoxy, in a thin-walled glass capillary. $\omega$ scans of several intense low-angle reflections had peak widths at half-height of 0.2°. Cell constants and axial photographs indicated that the crystal belonged to the triclinic system. Cell constants, determined at 23 °C using Mo K$\alpha$ (λ 0.710 730 Å) radiation, are $a$ = 10.936 (2) Å, $b$ = 11.170 (2) Å, $c$ = 8.871 (2) Å, $\alpha$ = 99.46 (1)°, $\beta$ = 98.56 (1)°, $\gamma$ = 108.58°, and $V$ = 989.4 (7) Å$^3$. The observed volume was consistent with that expected for $Z$ = 1.

The data were collected at 23 °C using a Syntex $P\bar{1}$ autodiffractometer and graphite crystal monochromatized Mo K$\alpha$ (λ 0.710 730 Å) radiation. Otherwise, data were collected as for I (see above). A total of 2600 unique reflections having 0° < $2\theta$(Mo K$\alpha$) ≤ 45.00° were collected. The intensities of three standard reflections were monitored frequently and showed no decrease over the period of data collection. The data were reduced to a set of relative $|F_o|^2$ values, and the 1565 observations having $|F_o|^2 > 3\sigma(|F_o|^2)$ were used in subsequent structure solution and refinement. Data were not corrected for absorption ($\mu$ = 6 $cm^{-1}$).

The space group was assumed to be $P\bar{1}$ (No. 2) and this was verified by the successful structure solution and refinement. The structure was solved by conventional heavy-atom methods.

The terminal diethylamino ligand is disordered with the methylene carbon atoms assumed to be distributed equally over two positions while the nitrogen atom and methyl groups are in the same positions for both orientations. The structure was refined to convergence using anisotropic thermal parameters for all nonhydrogen atoms except the carbon atoms in the axial $HNEt_2$ ligands.

Final unweighted and weighted residuals were 0.071 and 0.098, respectively. The esd of an observation weight was 2.07. A value of 0.07 was used for $\rho$ in the calculation of the weights. The largest peaks in the final difference Fourier map were in the region of the disordered axial ligands, presumably because of the anisotropic motion of the alkyl groups and additional disorder.

Tables of observed and calculated structure factors for both structures are available as supplementary material.

## Results and Discussion

**Synthesis.** Hydrocarbon solutions of $Cr(NEt_2)_4$ react rapidly with $CO_2$, even at −78 °C. In procedure 1 (see Experimental Section) the hydrocarbon solution of $Cr(NEt_2)_4$ is initially allowed to react *slowly* at room temperature with $CO_2$. Here the major chromium-containing species formed is a dark green, hydrocarbon-soluble, crystalline compound $Cr_2(O_2CNEt_2)_4(\mu\text{-}NEt_2)_2$, I. Compound I is inert to further reaction with $CO_2$ under these conditions. In procedure 2 the reaction is carried out by condensing $CO_2$ (>4 equiv) into a reaction flask containing the hydrocarbon solution of $Cr(NEt_2)_4$ cooled below −78 °C. The sealed system is then allowed to warm to room temperature. Here an initial rapid reaction occurs and the major chromium-containing product is a red, crystalline, hydrocarbon-soluble compound $Cr_2(O_2CNEt_2)_4 \cdot 2HNEt_2$, II. In both reaction procedures I and II are formed competitively along with another compound which is a pale blue-green, hydrocarbon-insoluble powder. The latter is a minor product and is believed to be polymeric $Cr(O_2CNEt_2)_3$. The only volatile organic species formed in these reactions are $Et_2NH$ and $EtN{=}CHMe$.

Aside from polymeric $CrF_4$, the only well-known compounds of quadrivalent chromium are $CrL_4$ compounds, where L is a $\beta$-elimination-stabilized alkyl, a dialkylamido, or a tertiary alkoxy ligand.[9] In this $CrL_4$ series chromium is always four-coordinate. All previous attempts to extend the $CrL_4$ series to give higher coordination numbers failed, and products of trivalent chromium were obtained, e.g., as in reactions 1[7] and 2[7,10] where R, R′ = alkyl or H.

$$2Cr(NEt_2)_4 + 8CS_2 \rightarrow 2Cr(S_2CNEt_2)_3 + (Et_2NC(S)S)_2 \quad (1)$$

$$2Cr(NEt_2)_4 + 7RR'CHOH \rightarrow 2Cr(OCHRR')_3 + 8HNEt_2 + RR'C{=}O \quad (2)$$

**Table I.** Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cr_2(O_2CNEt_2)_4(NEt_2)_2$[a]

| atom | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Cr | 0.07640 (8) | 0.1488 (1) | 0.23926 (8) | 0.00261 (4) | 0.0070 (1) | 0.00259 (4) | −0.0003 (2) | 0.00606 (9) | 0.0003 (2) |
| O(1) | 0.0967 (3) | 0.3261 (5) | 0.2406 (4) | 0.9031 (2) | 0.0074 (6) | 0.0036 (2) | −0.0001 (6) | −0.0006 (4) | 0.0006 (6) |
| O(2) | 0.1641 (3) | 0.1984 (6) | 0.2987 (4) | 0.0029 (2) | 0.0083 (6) | 0.0033 (2) | −0.0003 (6) | −0.0000 (4) | 0.0007 (7) |
| O(3) | 0.0950 (3) | −0.0284 (6) | 0.2342 (3) | 0.0034 (2) | 0.0089 (6) | 0.0030 (2) | 0.0001 (6) | 0.0005 (4) | 0.0013 (6) |
| O(4) | 0.1442 (3) | 0.0960 (6) | 0.1567 (4) | 0.0031 (2) | 0.0075 (6) | 0.0033 (2) | 0.0008 (7) | 0.0013 (4) | 0.0005 (6) |
| N(1) | 0.0097 (4) | 0.1501 (7) | 0.3276 (4) | 0.0029 (2) | 0.0082 (7) | 0.0024 (2) | −0.0000 (9) | −0.0003 (4) | −0.0000 (8) |
| N(2) | 0.1889 (5) | 0.4012 (7) | 0.3076 (5) | 0.0037 (3) | 0.0093 (8) | 0.0037 (3) | −0.0028 (9) | −0.0001 (5) | −0.0001 (9) |
| N(3) | 0.1644 (5) | −0.1066 (7) | 0.1434 (4) | 0.0049 (3) | 0.0080 (8) | 0.0031 (3) | 0.0030 (9) | 0.0014 (6) | 0.0001 (8) |

| atom | $x$ | $y$ | $z$ | $B$, Å$^2$ | atom | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| C(1) | 0.0167 (5) | 0.0376 (9) | 0.3739 (6) | 4.6 (2) | C(8) | 0.1695 (6) | 0.5278 (11) | 0.2904 (7) | 6.5 (3) |
| C(2) | 0.0835 (6) | 0.0362 (10) | 0.4223 (6) | 5.3 (2) | C(9) | 0.1255 (8) | 0.5823 (14) | 0.3535 (9) | 9.2 (4) |
| C(3) | 0.0139 (5) | 0.2640 (9) | 0.3721 (6) | 4.8 (2) | C(10) | 0.1344 (5) | −0.0125 (9) | 0.1781 (5) | 4.2 (2) |
| C(4) | −0.0393 (6) | 0.2680 (11) | 0.4383 (7) | 6.0 (3) | C(11) | 0.1514 (6) | −0.2308 (11) | 0.1662 (7) | 6.2 (3) |
| C(5) | 0.1503 (5) | 0.3080 (9) | 0.2820 (5) | 4.2 (2) | C(12) | 0.0922 (8) | −0.2873 (13) | 0.1199 (8) | 8.6 (4) |
| C(6) | 0.2531 (7) | 0.3737 (10) | 0.3486 (7) | 6.1 (3) | C(13) | 0.2067 (6) | −0.0846 (10) | 0.0768 (6) | 5.7 (3) |
| C(7) | 0.2366 (8) | 0.3470 (14) | 0.4306 (8) | 8.7 (4) | C(14) | 0.2664 (8) | −0.0973 (14) | 0.0942 (8) | 8.6 (4) |

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

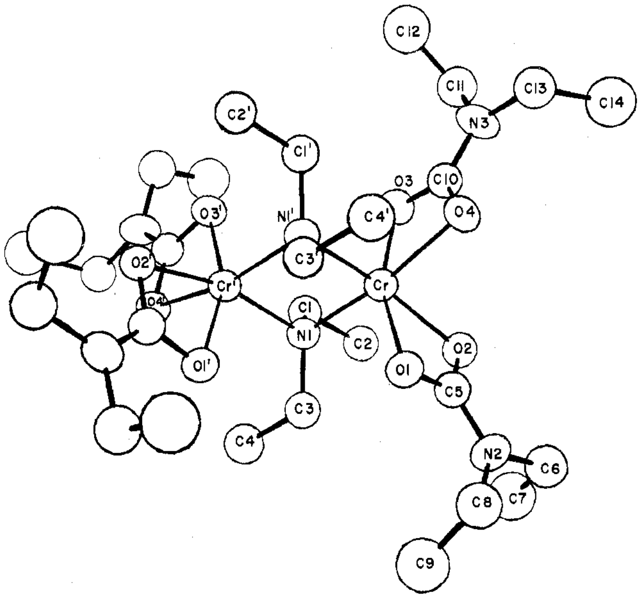
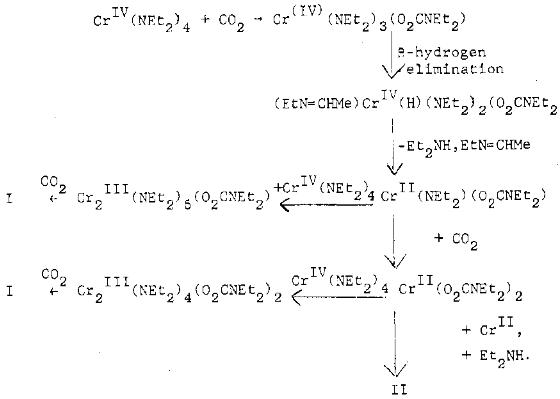


**Figure 1.** View of the $Cr_2(O_2CNEt_2)_4(\mu\text{-}NEt_2)_2$ molecule using 40% probability ellipsoids of thermal vibration representing the atoms and showing the atom labeling scheme. The molecule has $C_2$ symmetry.

**Scheme I**



The formation of trivalent chromium in the reaction between $Cr(NEt_2)_4$ and $CO_2$ is therefore not surprising, but the formation of divalent chromium products is most unexpected.

A plausible reaction pathway leading to the compound is given in Scheme I. Our proposal is that $CO_2$ insertion into a Cr–N bond of $Cr^{IV}(NEt_2)_4$ promotes β-hydrogen elimination from a coordinated diethylamido ligand, and then by reductive elimination of $Et_2NH$, a reactive divalent chromium species, $Cr^{II}(O_2CNEt_2)(NEt_2)$, is formed.[11] The subsequent reaction pathway is dependent on the relative concentration of $CO_2$. At low concentrations of $CO_2$, a reaction between $Cr^{II}(O_2CNEt_2)(NEt_2)$ and $Cr^{IV}(NEt_2)_4$ will lead to dimeric Cr(III) compounds and ultimately to I. At initial high $CO_2$ concentrations divalent chromium will predominate, and thus II will be the dominant product. Since the mechanism for $CO_2$ insertion into a $M{-}NR_2$ group involves electrophilic attack on the nitrogen lone pair, the bridging diethylamido ligands in I, which have quaternized nitrogens, are inert to further attack by $CO_2$.

**Structural Data.** Atomic parameters for $Cr_2(O_2CNEt_2)_4(NEt_2)_2$, I, and $Cr_2(O_2CNEt_2)_4{\cdot}2NHEt_2$, II, are presented in Tables I and II, respectively. ORTEP views of I and II depicting the atom labeling schemes are shown in Figures 1 and 3. Figure 2 shows a stereoview of I.

Compound I crystallizes in discrete dinuclear molecules in the orthorhombic space group *Pbcn* with $Z = 4$. Each molecule has crystallographic $C_2$ symmetry with the twofold axis bisecting the Cr–Cr′ and N(1)–N(1)′ vectors. The interatomic distances and angles are listed in Table III. The $Cr_2O_8N_2$ moiety has virtual $D_2$ symmetry and can be described as two octahedra sharing an edge. Each molecule is chiral,

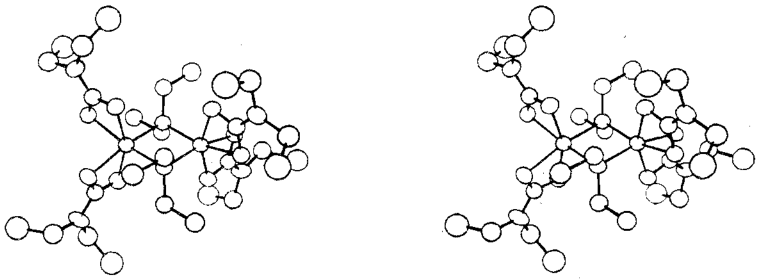


**Figure 2.** Stereoview of the $Cr_2(O_2CNEt_2)_4(\mu\text{-}NEt_2)_2$ molecule.

**Table II.** Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cr_2(O_2CNEt_2)_4 \cdot 2HNEt_2$[a]

| atom | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Cr | 0.0867 (1) | −0.0433 (1) | 0.0052 (1) | 0.0137 (1) | 0.0106 (1) | 0.0171 (1) | 0.0064 (2) | 0.0087 (2) | 0.0097 (2) |
| O(1) | 0.0334 (5) | −0.1076 (4) | 0.1927 (5) | 0.0165 (6) | 0.0156 (5) | 0.0198 (7) | 0.0109 (9) | 0.011 (1) | 0.018 (1) |
| O(2) | −0.1278 (5) | −0.0258 (5) | 0.1851 (5) | 0.0176 (6) | 0.0153 (5) | 0.0221 (7) | 0.0125 (9) | 0.018 (1) | 0.016 (1) |
| O(3) | 0.2097 (5) | 0.1296 (4) | 0.1398 (6) | 0.0140 (6) | 0.0121 (5) | 0.0255 (9) | 0.0033 (10) | 0.002 (1) | 0.009 (1) |
| O(4) | 0.0469 (5) | 0.2113 (4) | 0.1316 (6) | 0.0166 (6) | 0.0116 (5) | 0.0222 (8) | 0.0081 (9) | 0.010 (1) | 0.006 (1) |
| N(1) | −0.1036 (6) | −0.1449 (6) | 0.3615 (7) | 0.0179 (8) | 0.0134 (6) | 0.0184 (9) | 0.004 (1) | 0.012 (1) | 0.012 (1) |
| N(2) | 0.2551 (7) | 0.3418 (6) | 0.2396 (9) | 0.0180 (9) | 0.0118 (7) | 0.0335 (15) | 0.002 (1) | 0.004 (2) | 0.005 (2) |
| N(3) | 0.2595 (9) | −0.1396 (9) | 0.0153 (11) | 0.0334 (12) | 0.0386 (12) | 0.0315 (17) | 0.047 (2) | −0.003 (2) | 0.012 (2) |
| C(1) | −0.0636 (7) | −0.0919 (7) | 0.2408 (8) | 0.0163 (9) | 0.0119 (7) | 0.016 (1) | 0.005 (1) | 0.008 (2) | 0.011 (1) |
| C(2) | −0.0325 (9) | −0.2170 (8) | 0.4323 (9) | 0.0256 (13) | 0.0170 (8) | 0.022 (1) | 0.016 (2) | 0.007 (2) | 0.022 (2) |
| C(3) | −0.0799 (13) | −0.3579 (10) | 0.3438 (15) | 0.0404 (20) | 0.0186 (11) | 0.040 (2) | 0.029 (2) | 0.012 (4) | 0.011 (3) |
| C(4) | −0.2117 (8) | −0.1242 (8) | 0.4225 (9) | 0.0191 (10) | 0.0194 (11) | 0.023 (1) | 0.006 (2) | 0.021 (2) | 0.013 (2) |
| C(5) | −0.3442 (11) | −0.2238 (13) | 0.3378 (15) | 0.0213 (15) | 0.0333 (20) | 0.042 (3) | 0.009 (3) | 0.013 (3) | 0.009 (4) |
| C(6) | 0.1666 (8) | 0.2224 (7) | 0.1650 (9) | 0.0159 (10) | 0.0117 (8) | 0.019 (1) | 0.002 (1) | 0.003 (2) | 0.006 (2) |
| C(7) | 0.2098 (11) | 0.4507 (9) | 0.2743 (14) | 0.0283 (17) | 0.0154 (11) | 0.045 (3) | 0.012 (2) | 0.001 (4) | 0.013 (3) |
| C(8) | 0.2019 (18) | 0.5073 (14) | 0.1544 (22) | 0.0484 (30) | 0.0311 (20) | 0.079 (5) | 0.031 (4) | 0.042 (6) | 0.033 (5) |
| C(9) | 0.3979 (10) | 0.3595 (10) | 0.2834 (14) | 0.0182 (13) | 0.0172 (12) | 0.046 (3) | −0.000 (2) | 0.001 (3) | −0.006 (3) |
| C(10) | 0.4522 (13) | 0.3797 (13) | 0.1373 (17) | 0.0298 (18) | 0.0314 (20) | 0.059 (3) | 0.014 (3) | 0.039 (4) | 0.013 (4) |

| atom | $x$ | $y$ | $z$ | $B$, Å$^2$ | atom | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| C(11B)[b] | 0.378 (2) | −0.077 (2) | 0.123 (3) | 12.3 (7) | C(13A)[b] | 0.319 (3) | −0.142 (2) | −0.125 (3) | 12.4 (8) |
| C(11A)[b] | 0.317 (3) | −0.151 (3) | 0.135 (4) | 15.1 (10) | C(13B)[b] | 0.215 (3) | −0.267 (2) | −0.138 (3) | 12.5 (8) |
| C(12) | 0.356 (1) | −0.068 (1) | 0.280 (2) | 12.8 (4) | C(14) | 0.240 (2) | −0.222 (2) | −0.245 (2) | 16.0 (5) |

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Refined at 0.5 occupancy.

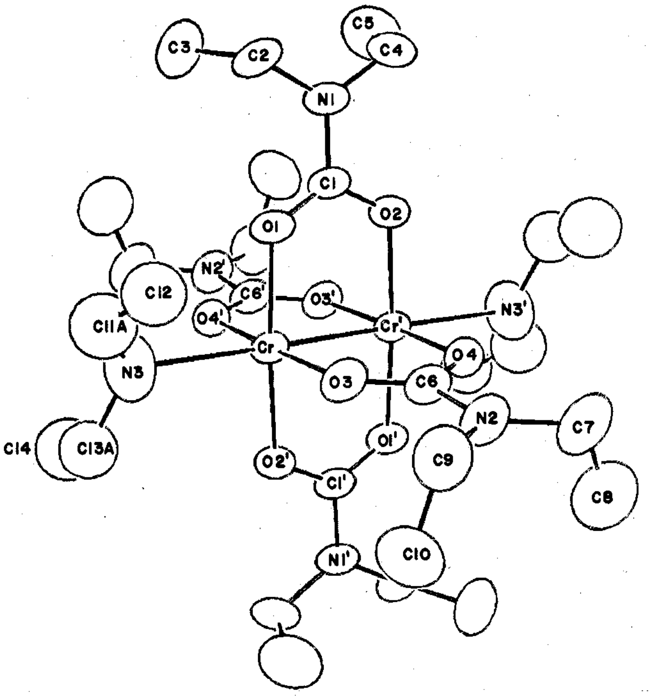


Figure 3. View of the $Cr_2(O_2CNEt_2)_4 \cdot 2HNEt_2$ molecule using 30% probability ellipsoids and showing the atom labeling scheme. Only one orientation of the disordered methylene groups on N(3) is shown. The molecule has a center of inversion at the midpoint of the Cr–Cr bond.

**Table III.** Bond Distances (Å) and Angles (deg) in $Cr_2(O_2CNEt_2)_4(NEt_2)_2$[a]

| | | | |
|---|---|---|---|
| | Distances | | |
| Cr–Cr′ | 2.948 (2) | C(5)–O(1) | 1.285 (8) |
| –O(1) | 1.993 (4) | –O(2) | 1.273 (8) |
| –O(2) | 2.066 (5) | –N(2) | 1.347 (8) |
| –O(3) | 1.988 (5) | N(2)–C(6) | 1.47 (1) |
| –O(4) | 2.063 (4) | –C(8) | 1.48 (1) |
| –N(1) | 2.046 (5) | C(6)–C(7) | 1.55 (1) |
| –N(1)′ | 2.045 (5) | C(8)–C(9) | 1.54 (1) |
| N(1)–N(1)′ | 2.84 (1) | O(3)–O(4) | 2.177 (6) |
| –C(1) | 1.503 (8) | C(10)–O(3) | 1.277 (8) |
| –C(3) | 1.494 (8) | –O(4) | 1.272 (8) |
| C(1)–C(2) | 1.55 (1) | –N(3) | 1.342 (8) |
| C(3)–C(4) | 1.57 (1) | N(3)–C(11) | 1.45 (1) |
| O(1)–O(2) | 2.179 (6) | –C(13) | 1.47 (1) |
| | | C(11)–C(12) | 1.54 (1) |
| | | C(13)–C(14) | 1.56 (1) |
| | Angles | | |
| Cr′–Cr–O(1) | 101.0 (1) | Cr′–N(1)–C(1) | 113.3 (4) |
| –O(2) | 137.4 (1) | –C(3) | 111.6 (4) |
| Cr′–Cr–O(3) | 100.6 (1) | C(1)–N(1)–C(3) | 112.8 (5) |
| –O(4) | 135.9 (2) | N(1)–C(1)–C(2) | 113.4 (6) |
| –N(1) | 43.9 (2) | N(1)–C(3)–C(4) | 113.6 (6) |
| –N(1)′ | 43.9 (2) | Cr–O(1)–C(5) | 90.6 (4) |
| O(1)–Cr–O(2) | 64.9 (2) | Cr–O(2)–C(5) | 87.7 (4) |
| –O(3) | 158.4 (2) | O(1)–C(5)–O(2) | 116.8 (7) |
| –O(4) | 99.4 (2) | N(2)–C(5)–O(1) | 121.2 (7) |
| –N(1) | 96.0 (2) | –O(2) | 122.0 (7) |
| O(1)–Cr–N(1)′ | 99.1 (2) | C(5)–N(2)–C(6) | 118.3 (7) |
| O(2)–Cr–O(3) | 98.0 (2) | –C(8) | 120.7 (7) |
| –O(4) | 86.7 (2) | C(6)–N(2)–C(8) | 120.8 (7) |
| –N(1) | 95.5 (2) | N(2)–C(6)–C(7) | 110.8 (8) |
| –N(1)′ | 163.9 (2) | N(2)–C(8)–C(9) | 110.4 (8) |
| O(3)–Cr–O(4) | 65.0 (2) | Cr–O(3)–C(10) | 90.4 (4) |
| –N(1) | 98.9 (2) | Cr–O(4)–C(10) | 87.2 (4) |
| –N(1)′ | 97.1 (2) | O(3)–C(10)–O(4) | 117.3 (7) |
| O(4)–Cr–N(1) | 163.8 (2) | N(3)–C(10)–O(3) | 121.3 (7) |
| –N(1)′ | 94.5 (2) | –O(4) | 121.4 (7) |
| N(1)–Cr–N(1)′ | 87.8 (2) | C(10)–N(3)–C(11) | 121.4 (7) |
| Cr–N(1)–Cr′ | 92.2 (2) | –C(13) | 119.5 (7) |
| –C(1) | 112.0 (4) | C(11)–N(3)–C(13) | 118.9 (6) |
| –C(3) | 113.3 (4) | N(3)–C(11)–C(12) | 110.6 (8) |
| | | N(3)–C(13)–C(14) | 110.9 (7) |

[a] Atoms are labeled as in Figure 1. Estimated standard deviations in the least significant digits are in parentheses.

and there are two molecules of each enantiomorph in the unit cell, those of opposite hand related by the inversion centers and those of the same hand related by the screw axes.

The "octahedral" coordination about the chromium atom is, of course, distorted by the short "bite" of the bidentate carbamato ligands which is only 2.178 (6) Å whereas an edge of the coordination octahedron should be ca. 2.87 Å. The bidentate ligands are evidently spanning edges of the idealized octahedra since the angles between the N(1)/Cr/N(1)′, O(1)/Cr/O(2), and O(3)/Cr/O(4) planes range from 85 to 95°. As expected, each of the $CrO_2CNC_2$ moieties is essentially planar, as is the central $Cr_2N_2$ moiety. The diethylamido groups symmetrically bridge the chromium atoms, while the bidentate carbamato ligands are bonded slightly asymmetrically. The two Cr–O distances (2.066 (5) and 2.063

**Table IV.** Bond Distances (Å) and Angles (deg) in $Cr_2(O_2CNEt_2)_4 \cdot 2HNEt_2$

| Distances | | | |
|---|---|---|---|
| Cr–Cr′ | 2.384 (2) | C(6)–O(4) | 1.259 (7) |
| –O(1) | 2.009 (4) | –N(2) | 1.361 (7) |
| –O(2)′ | 2.019 (4) | N(2)–C(7) | 1.458 (10) |
| –O(3) | 2.018 (4) | –C(9) | 1.492 (10) |
| –O(4)′ | 2.026 (4) | C(7)–C(8) | 1.329 (15) |
| –N(3) | 2.452 (8) | C(9)–C(10) | 1.524 (13) |
| C(1)–O(1) | 1.252 (7) | N(3)–C(11A) | 1.20 (3) |
| –O(2) | 1.276 (7) | –C(11B) | 1.38 (3) |
| –N(1) | 1.368 (7) | –C(13A) | 1.49 (2) |
| N(1)–C(2) | 1.437 (8) | –C(13B) | 1.68 (2) |
| –C(4) | 1.438 (8) | C(11)A–C(12) | 1.38 (3) |
| C(2)–C(3) | 1.521 (10) | C(11)B–C(12) | 1.45 (3) |
| C(4)–C(5) | 1.509 (11) | C(13)A–C(14) | 1.27 (2) |
| C(6)–O(3) | 1.271 (8) | C(13)B–C(14) | 1.18 (2) |

| Angles | | | |
|---|---|---|---|
| Cr′–Cr–O(1) | 87.7 (1) | C(2)–N(1)–C(4) | 119.9 (5) |
| –O(2)′ | 87.8 (1) | N(1)–C(2)–C(3) | 112.2 (6) |
| –O(3) | 88.2 (1) | N(1)–C(4)–C(5) | 113.1 (7) |
| –O(4)′ | 87.8 (1) | Cr–O(3)–C(6) | 119.1 (4) |
| –N(3) | 178.1 (3) | Cr′–O(4)–C(6) | 119.2 (4) |
| O(1)–Cr–O(2)′ | 175.5 (2) | O(3)–C(6)–O(4) | 124.8 (6) |
| –O(3) | 91.9 (2) | –N(2) | 117.9 (7) |
| –O(4) | 88.2 (2) | O(4)–C(6)–N(2) | 117.2 (7) |
| O(2)′–Cr–O(3) | 88.4 (2) | C(6)–N(2)–C(7) | 119.8 (7) |
| –O(4)′ | 91.1 (2) | –C(9) | 119.2 (7) |
| O(3)–Cr–O(4)′ | 176.0 (2) | C(7)–N(2)–C(9) | 120.9 (6) |
| N(3)–Cr–O(1) | 91.2 (3) | N(2)–C(7)–C(8) | 112 (1) |
| –O(2)′ | 93.3 (3) | N(2)–C(9)–C(10) | 105.7 (8) |
| –O(3) | 93.5 (3) | Cr–N(3)–C(11A) | 123 (2) |
| –O(4)′ | 90.5 (3) | –C(11B) | 120 (1) |
| Cr–O(1)–C(1) | 121.0 (4) | Cr–N(3)–C(13A) | 114 (1) |
| Cr′–O(2)–C(1) | 119.8 (4) | –C(13B) | 109 (1) |
| O(1)–C(1)–O(2) | 123.4 (5) | C(11A)–N(3)–C(13A) | 120 (2) |
| –N(1) | 119.7 (6) | C(11B)–N(3)–C(13B) | 131 (1) |
| O(2)–C(1)–N(1) | 116.8 (6) | N(3)–C(11A)–C(12) | 128 (3) |
| C(1)–N(1)–C(2) | 120.7 (6) | N(3)–C(11B)–C(12) | 111 (2) |
| –C(4) | 120.7 (6) | N(3)–C(13A)–C(14) | 112 (2) |
| | | N(3)–C(13B)–C(14) | 105 (2) |

(5) Å) which are "trans" to nitrogen (N–Cr–O = 164°) are 0.074 Å longer than the Cr–O distances (1.993 (4) and 1.988 (5) Å) which are "cis" (O–Cr–N = 98°) to nitrogen. This type of trans effect has been noted previously in mononuclear $M(NMe_2)_m(O_2CNMe_2)_n$ compounds.[1,3]

The long Cr–Cr distance of 2.948 (2) Å is consistent with the conclusion that no significant Cr–Cr bonding interaction exists. The compound is paramagnetic and shows strong antiferromagnetic coupling as evidenced by the marked reduction in $\mu_{eff}$ from the spin-only value and the temperature-dependent properties of $\mu_{eff}$. It is particularly interesting to note that the closely related molybdenum compound $Mo_2(NMe_2)_2(O_2CNMe_2)_4$[12a] is diamagnetic and believed to contain a Mo-to-Mo triple bond with a structure akin to that found for $W_2Me_2(O_2CNEt_2)_4$.[12b] This provides a good example of how, for the group 6 metals in their trivalent state, metal-to-metal bonding increases down the series; cf. the $M_2Cl_9^{3-}$ ions which have the confacial bioctahedral structure where the metal-to-metal distances are 3.12, 2.67, and 2.45 Å for Cr, Mo, and W, respectively.[13]

Compound II crystallizes in discrete dinuclear molecules in the triclinic space group $P\bar{1}$ with $Z = 1$, and the molecule has crystallographically imposed $C_i$ symmetry. Table IV lists bond length and angles. The compound has four bridging carbamato ligands and two axially coordinated molecules of diethylamine. This type of structure, $Cr(O-O)_4L_2$, is typical of dichromium tetracarboxylates. The $Cr_2O_8N_2$ core has essentially $D_{4h}$ symmetry. The average Cr–O distance of 2.018 (7) Å is in the range found for $Cr_2(O_2CR)_4L_2$ compounds.

The rough inverse correlation between Cr–Cr distances and Cr–L axial distances has been noted for $Cr_2(O_2CR)_4L_2$ compounds.[14] The Cr–Cr distance we find for II is somewhat longer than might be expected from the axial Cr–N distance of 2.452 (8) Å. The point for this compound is, in fact, close to that for $Cr_2(O_2CCMe_3)_4$, and both lie well away from the region expected on the basis of the structure for about a dozen other compounds. The fact that the axial donor here is an aliphatic amine nitrogen atom may be one cause of the unexpectedly long Cr–Cr bond, but perhaps the only safe comment is that this structure provides further evidence that length of a Cr–Cr quadruple bond is extremely sensitive to the properties of the ligands surrounding it.

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**Registry No.** I, 67951-81-9; II, 67941-31-5; $Cr(NEt_2)_4$, 67938-78-7; $CO_2$, 124-38-9.

**Supplementary Material Available:** Table of observed and calculated structure factors for $Cr_2(O_2CNEt_2)_4 \cdot 2HNEt_2$ and $Cr_2(O_2CNEt_2)_4(\mu\text{-}NEt_2)_2$ (14 pages). Ordering information is given on any current masthead page.

## References and Notes

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