(2) B. E. Svenningsen and R. G. Hazell, personal communication, 1977.
(3) F. Grundtvig and A. Hordvik, *Acta Chem. Scand.*, **25**, 1567 (1971).
(4) (a) A. Hordvik and J. Sletten, *Acta Chem. Scand.*, **20**, 1907 (1966); (b) *ibid.*, **20**, 1935 (1966).
(5) A. Zalkin, T. E. Hopkins, and D. H. Templeton, *Inorg. Chem.*, **5**, 1767 (1966).
(6) B. Kreiss and M. L. Ziegler, *Z. Anorg. Allg. Chem.*, **388**, 158 (1972).
(7) B. Kreiss and M. L. Ziegler, *Z. Naturforsch. B*, **27**, 1282 (1972).
(8) A. Hordvik, *Q. Rep. Sulfur Chem.*, **5**, 21 (1970).
(9) R. E. Rosenfield, Jr., R. Parthasarathy, and J. D. Dunitz, *J. Am. Chem. Soc.*, **99**, 4860 (1977).
(10) B. A. W. Cordes, R. F. Kruh, and E. K. Gordon, *Inorg. Chem.*, **4**, 681 (1965).
(11) C. M. Mikulski, P. J. Russo, M. S. Saran, A. G. MacDiarmid, A. F. Garito, and A. J. Heeger, *J. Am. Chem. Soc.*, **97**, 6358 (1975).
(12) K. Bechgaard, T. J. Kistenmacher, A. N. Bloch, and D. O. Cowan, *Acta Crystallogr., Sect. B*, **33**, 417 (1977).
(13) W. L. Jolly and K. D. Maguire, *Inorg. Synth.*, **9**, 103 (1967).
(14) R. H. Blessing, P. Coppens, and P. Becker, *J. Appl. Crystallogr.*, **7**, 488 (1974).
(15) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(16) P. Coppens, Y. W. Yang, R. H. Blessing, W. F. Cooper, and F. K. Larsen, *J. Am. Chem. Soc.*, **99**, 760 (1977).
(17) J. W. Bats, P. Coppens, and T. F. Koetzle, *Acta Crystallogr., Sect. B*, **33**, 37 (1977).
(18) M. L. DeLucia and P. Coppens, to be submitted for publication.

Contribution from the Department of Chemistry,
University of Victoria, Victoria,
British Columbia, Canada V8W 2Y2

Synthesis of *cis*- and *trans*-$[Cr(en)_2(NH_3)_2]^{3+}$ and $[Cr(en)(NH_3)_4]^{3+}$

C. F. C. Wong and A. D. Kirk*

Received August 23, 1977

Only a few complexes of chromium(III) with mixed amine ligands have been reported,[1,4] few of these contain only neutral ligands,[1] and no general synthetic methods for their preparation exist. We wish to report the synthesis of *cis*- and *trans*-$[Cr(en)_2(NH_3)_2]^{3+}$ and $[Cr(en)(NH_3)_4]^{3+}$ and their spectral properties.

The most obvious route to compounds of this type is ammonolysis of acido-ethylenediamine starting materials in liquid ammonia. Prior studies of the reactions of acidochromium(III) complexes in liquid ammonia have shown, however, that thermal substitution with trans → cis stereochemical rearrangement is of common occurrence,[5] suggesting that although preparation of *cis*-$[Cr(en)_2(NH_3)_2]^{2+}$ would probably be straightforward, the trans isomer would be more difficult.

In agreement with our expectations we found that *cis*-$[Cr(en)_2Cl_2]^+$ reacted smoothly in liquid ammonia at low temperature to yield $[Cr(en)_2(NH_3)_2]^{3+}$, with a few percent trans (ca. 3% ?). Both *trans*-$[Cr(en)_2Br_2]^+$ and *trans*-$[Cr(en)_2Cl_2]^+$, however, reacted with almost complete isomerization to yield about 95% *cis*-$[Cr(en)_2(NH_3)_2]^{3+}$.

A reasonable yield of the trans compound was finally achieved by ammonolysis of the more inaccessible compound *trans*-$[Cr(en)_2NH_3Cl]^{2+}$, the synthesis of which has been previously reported.[5] This reaction gave approximately one-third trans product.

Since $[Cr(en)X_4]^-$ compounds, where X is an easily substituted acido ligand, are not available to prepare $[Cr(en)(NH_3)_4]^{3+}$, a three-stage synthesis was required starting with $[Cr(en)(NH_3)H_2OCl_2]^+$ and involving the steps

$$[Cr(en)(NH_3)H_2OCl_2]^+ \xrightarrow[NH_3]{\text{liquid}} [Cr(en)(NH_3)_3H_2O]^{3+}$$

$$[Cr(en)(NH_3)_3H_2O]Br_3 \xrightarrow{\Delta} [Cr(en)(NH_3)_3Br]Br_2$$

$$[Cr(en)(NH_3)_3Br]^{2+} \xrightarrow[NH_3]{\text{liquid}} [Cr(en)(NH_3)_4]^{3+}$$

Table I. UV-Visible Spectral Data for $[Cr(en)_n(NH_3)_{6-2n}]^{3+}$ Complexes

Complex^a	λ_{max}^{b}	λ_{min}	λ_{max}^{b}	Ref
$[Cr(NH_3)_6]^{3+}$	351 (32.7)	395 (7.3)	463 (39.4)	9
	354 (33.7)		466 (40.7)	10
	350 (32)	395 (8.7)	462 (39)	11
$[Cr(en)(NH_3)_4]^{3+}$	351 (42.4	396 (9.8)	462 (51.0)	This work
trans-$[Cr(en)_2(NH_3)_2]^{3+}$	347 (36.7)	391 (9.5)	454 (47.0)	This work
cis-$[Cr(en)_2(NH_3)_2]^{3+}$	351 (53.7)	395 (13.0)	460 (65.8)	This work
$[Cr(en)_3]^{3+}$	350 (61.3)	394 (13.9)	456 (75.7)	9
	351 (60.7)		457 (76.5)	12

^{a} All solutions were in 0.1 N HCl. ^{b} Absorption wavelengths in nm. Values in parentheses are the molar absorptivities.

The compounds were characterized by elemental analysis and by measurement of their UV–visible and infrared spectra. The UV–visible spectral data, Table I, are consistent with expectations based on ligand field theory and an analogy to the parent complexes, $[Cr(NH_3)_6]^{3+}$ and $[Cr(en)_3]^{3+}$. The two $[Cr(en)_2(NH_3)_2]^{3+}$ isomers were carefully separated by fractional crystallization and were distinguishable by (1) their different crystal habits, (2) their UV–visible spectra, for which the molar absorptivity of the cis isomer was about 40% higher than for the trans, consistent with the trend found for a number of $[Cr(en)_2(NH_3)X]^{n+}$ isomer pairs,[5] and (3) the infrared band patterns[6] in the region between 600 and 300 cm^{-1} where the cis isomer shows bands at 548 (s), 527 (ms), 473 (m), 450 (m), and 410 (w) and the trans isomer bands at 560 (m), 543 (sh), 479 (m), and 430 (m). Although we have experienced no difficulties in our laboratory with these compounds, it is appropriate to draw attention to the fact that the perchlorate salts are potentially very explosive and could show great sensitivity to heat or shock under some circumstances.

$[Cr(en)(NH_3)_3H_2O]Br_3$. $[Cr(en)(NH_3)(H_2O)Cl_2]Cl$[7] was reacted with dried distilled liquid ammonia (ca. 1 mL/g of complex) in a sealed Carius tube at 20 °C for ca. 0.5 h. The dried purple product (6.0 g) was dissolved in a minimum of 0.1 M HBr and one volume of 48% HBr was added. The color of the solution changed from purple to a deep orange-red, and upon addition of acetone to the solution and cooling to 0 °C, a pale orange precipitate formed. This fraction (1.5 g) was removed by filtration, washed with acetone, and dried in a desiccator. A second fraction (1.5 g), slightly more orange than the first was obtained with further addition of acetone to the filtrate. The two fractions exhibited different solubilities and different solid-state anation behaviors (see later) and are likely to correspond to the different isomers of $[Cr(en)(NH_3)_3H_2O]Br_3$. The UV-visible absorption maxima of fraction 1 were 359 and 469 nm, consistent with expectations based on ligand field theory and analogy to $[Cr(NH_3)_5H_2O]^{3+}$ and *cis*- and *trans*-$[Cr(en)_2(NH_3)H_2O]^{3+}$. Since $[Cr(en)(NH_3)_3H_2O]Br_3$ was to be used only as an intermediate, no further attempts were made to establish the chemical purity or isomer nature of the fractions obtained.

$[Cr(en)(NH_3)_3Br]Br_2$. This was prepared by the solid-state anation of $[Cr(en)(NH_3)_3H_2O]Br_3$. Fractions 1 and 2 obtained above were heated and the positions of the UV–visible absorption maxima followed. After 24 h at 70 °C, these were 372 and 486 nm for fraction 1 and 377 and 510 nm for fraction 2. After further heating at 90 °C for 2 h, the absorption maxima for fraction 1 changed to 374 and 497 nm, while no change was observed for fraction 2. Fraction 1 was heated at 90 °C for a further 2 h and the two fractions were combined. No attempt was made to establish the purity or isomer nature of the sample as the compound was to be used only as an intermediate.

$[Cr(en)(NH_3)_4](ClO_4)_3 \cdot H_2O$. $[Cr(en)(NH_3)_3Br]Br_2$ was reacted with liquid ammonia (ca. 1 mL/g) in a sealed Carius

0020-1669/78/1317-1672$01.00/0 © 1978 American Chemical Society

tube at 20 °C for 1 h. For conversion to the perchlorate salt, a 1.0-g sample of the dried crude product was dissolved in 2 mL of 0.1 N HCl, 2 mL of methanol was added, 60% $HClO_4$ was added dropwise to the point of incipient precipitation, and the solution was cooled to 0 °C. The yellow product (with a slight orange tint due to $[Cr(en)_2(NH_3)_3H_2O](ClO_4)_3)$ was filtered off, washed with methanol and then with ether, and air-dried (yield 1.0 g, ca. 90%). The crude perchlorate salt was purified by fractional recrystallization. Spectral data are given in Table I. Anal. Calcd for $[Cr(en)(NH_3)_4](ClO_4)_3\cdot H_2O$: Cr, 10.47; C, 4.84; H, 4.66; N, 16.92. Found: Cr, 10.8; C, 5.0; H, 4.5; N, 17.0.

***cis*-$[Cr(en)_2(NH_3)_2](ClO_4)_3$.** *cis*-$[Cr(en)_2Cl_2]ClO_4$, prepared as described by Rollinson and Bailar,[8] was reacted with ammonia (ca. 2 mL/g of starting material) at 20 °C for 2 h. The crude $[Cr(en)_2(NH_3)_2]Cl_2ClO_4$ product was >97% cis as based on the UV–visible spectrum. For replacement of the chloride counterion and for recrystallization, a 3-g sample was dissolved in 0.01 N HCl (12 mL) at 30 °C and the solution was filtered. Then 4 mL of 60% $HClO_4$ was added to the filtrate followed by methanol added dropwise until a small amount of precipitate was formed. The solution was again filtered to remove any trans product and then cooled to 0 °C to give fraction 1. This was filtered off, washed with a small amount of methanol followed by ether, and dried in vacuo. Fraction 2 was obtained in the same manner subsequent to the further addition of two volumes of methanol to the filtrate. Chromium determinations on fractions 1 and 2 indicated counterion purity had not been achieved (expected value 10.3% for the triperchlorate salt; found 12.6 and 12.0%, respectively) by the single recrystallization. About three or four similar recrystallizations were necessary to give analytically pure triperchlorate. Spectral data are given in Table I.

Anal. Calcd for $[Cr(en)_2(NH_3)_2](ClO_4)_3$: Cr, 10.30; C, 9.54; H, 4.39; N, 16.65. Found: Cr, 10.4; C, 9.7; H, 4.3; N, 16.5.

***trans*-$[Cr(en)_2(NH_3)_2](ClO_4)_3\cdot H_2O$.** *trans*-$[Cr(en)_2(NH_3)Cl](ClO_4)_3$, prepared as described earlier,[5] except that the thermal anation was accomplished by heating at 70 °C for 24 h, was reacted with liquid ammonia (ca. 1 g to 1 mL) at 20 °C for 1 h in a sealed Carius tube. The crude material was a mixture of *cis-/trans-*$[Cr(en)_2(NH_3)_2]Cl(ClO_4)_2$, approximately 2:1 based on the UV–visible spectrum.

The trans isomer was isolated by fractional recrystallization. The crude mixture (1 g) was dissolved in 2 mL of 0.1 N HCl, and 0.5 mL of 60% $HClO_4$ was added. The solution was cooled to −5 °C to initiate crystallization and the pale yellow precipitate filtered off, washed with 2 mL of methanol followed by ether, and air-dried. The yield of crude *trans*-$[Cr(en)_2(NH_3)_2](ClO_4)_3$ was 0.11 g. The filtrate could be treated with methanol (20 mL) to recover most (ca. 0.70 g) of the remaining complex(es).

In a subsequent fractional recrystallization, crystals of the crude trans material were used to seed the solution. The crude trans product was recrystallized by dissolving in warm (30 °C) 0.1 N HCl (ca. 6 mL/g), adding 60% $HClO_4$ (ca. 1 mL/g), and cooling to 0 °C. The yellow platelets were filtered, washed with 5 mL of ice-cold 2 M $HClO_4$, 50/50 methanol/ether, and ether, and air-dried. The yield was about 0.75 g/g of the crude product. Spectral data are given in Table I.

Anal. Calcd for $[Cr(en)_2(NH_3)_2](ClO_4)_3\cdot H_2O$: Cr, 9.95; C, 9.19; H, 4.63; N, 15.92. Found: Cr, 10.1; C, 9.4; H, 4.6; N, 15.9.

The water of crystallization could be removed by heating the sample at 50 °C for 1 h.

Acknowledgment. The authors wish to thank the National Research Council of Canada and the University of Victoria for financial support.

Registry No. $[Cr(en)(NH_3)_4](ClO_4)_3$, 65982-67-4; *cis*-$[Cr(en)_2(NH_3)_2](ClO_4)_3$, 66008-06-8; *trans*-$[Cr(en)_2(NH_3)_2](ClO_4)_3$, 65982-65-2; $[Cr(en)(NH_3)_3(H_2O)]Br_3$, 65982-73-2; $[Cr(en)(NH_3)(H_2O)Cl_2]Cl$, 16702-52-6; $[Cr(en)(NH_3)_3Br]Br_2$, 65982-72-1; *cis*-$[Cr(en)_2Cl_2]ClO_4$, 15654-71-4; *trans*-$[Cr(en)_2(NH_3)Cl](ClO_4)_2$, 58437-87-9.

References and Notes

(1) P. Pfeiffer, T. Grassman, and H. Pietch, *Z. Anorg. Chem.*, **57**, 312 (1908).
(2) C. S. Garner and D. A. House, *Transition Met. Chem.*, **6**, 59 (1970).
(3) J. W. Vaughn and G. J. Seiler, *Inorg. Chem.*, **13** 598 (1974).
(4) D. A. House, *Inorg. Nucl. Chem. Lett.*, **12**, 259 (1976).
(5) C. F. C. Wong and A. D. Kirk, *Can. J. Chem.*, **53**, 3388 (1976).
(6) M. N. Hughes and W. R. McWhinnie, *J. Chem. Soc. A*, 592 (1967).
(7) D. A. House, R. G. Hughes, and C. S. Garner, *Inorg. Chem.*, **6**, 1077 (1967).
(8) C. L. Rollinson and J. C. Bailar, *Inorg. Synth.*, **2**, 201 (1946).
(9) C. F. C. Wong and A. D. Kirk, unpublished results.
(10) M. R. Edelson and R. A. Plane, *Inorg. Chem.*, **3**, 231 (1964).
(11) Estimated from the spectral curve of K. G. Paulsen and C. S. Garner, *J. Am. Chem. Soc.*, **81**, 2615 (1959).
(12) F. Woldbye, *Acta Chem. Scand.*, **12**, 1079 (1958).

Contribution from the Department of Chemistry,
Princeton University, Princeton, New Jersey 08540

In Search of Metal–Metal Metathesis in the Chemistry of Compounds Containing Metal-to-Metal Triple Bonds between Molybdenum and Tungsten Atoms

M. H. Chisholm,* M. W. Extine, R. L. Kelly, W. C. Mills,
C. A. Murillo, L. A. Rankel, and W. W. Reichert

Received October 11, 1977

The occurrence of transition-metal complexes containing metal-to-metal multiple bonds is now well documented.[1] Scores of such compounds have been structurally characterized and several have been subjected to detailed spectroscopic examination. Recently X_α–SW calculations have been carried out on compounds containing M–M bonds of order 3[2] and 4[3-5] and the results have been correlated with the observed spectroscopic data. Despite the emergence of a basic understanding of the electronic structure of these compounds little is known about (i) the mechanisms of their formation and (ii) the relationships that exist between the formation/existence of dinuclear compounds with M–M multiple bonds and cluster or polynuclear compounds of the same empirical formula.

We have sought to gain insight into some of these mystiques by looking for the formation of heterodinuclear compounds containing M–M′ multiple bonds. We report here some findings relating to compounds containing triple bonds between molybdenum and tungsten atoms.

Results and Discussion

M_2L_6 Compounds (M = Mo, W; L = R (alkyl), NR_2). Recent work has established a structurally related series of compounds of general formula M_2L_6, where M = Mo and W and L = R (β-elimination-stabilized alkyl),[6,7] NR_2[8,9] and OR.[10,11] The alkyls and dialkylamides are formed in metathetic reactions represented by eq 1–4; the alkoxides are formed by alcoholysis reactions involving the dialkylamides.

The nature of these reactions (eq 1–4) is clearly complex. It has been suggested[15] that the dinuclear compounds might arise from the coupling of two reactive mononuclear species, eq 5.

0020-1669/78/1317-1673$01.00/0 © 1978 American Chemical Society