611. *Studies on Transition-metal–Nitric Oxide Complexes. Part VII.*[1] *Nitric Oxide Complexes of Chromium and Molybdenum.*

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A number of octahedral nitrosyl complexes of chromium and molybdenum have been prepared and their structures have been examined by means of spectroscopic and magnetochemical methods.

(A) *Chromium Nitrosyl Complexes.*—The known nitrosyl complexes of chromium are $[Cr^{I}(CN)_5NO]^{3-}$,[2] $[Cr(NO)(H_2O)_5]^{2+}$,[3] the dithiocarbamates $(R_2NCS_2)_2Cr^{0}(NO)_2$,[4] and some cyclopentadienyl derivatives of chromium(0).[5]

1. *Potassium pentacyanonitrosylchromate*(0), $K_4[Cr^{0}(CN)_5NO]$. It has previously been shown [2] that polarographic reduction of $[Cr^{I}(CN)_5NO]^{3-}$ at the dropping-mercury electrode gives a reversible one-electron cathodic wave [$E_{\frac{1}{2}} = -0{\cdot}95$ v against the standard calomel electrode (S.C.E.)] which presumably corresponds to the reaction

$$[Cr^{I}(CN)_5NO]^{3-} + e^- \longrightarrow [Cr^{0}(CN)_5NO]^{4-}$$

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[1] Part VI, Griffith, Lewis, and Wilkinson, *J.*, 1961, 775.

[2] Griffith, Lewis, and Wilkinson, *J.*, 1959, 872.

[3] Ardon and Herman, *J.*, 1962, 507.

[4] Malatesta, *Gazzetta*, 1940, **70**, 729.

[5] Piper and Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **2**, 38, 104, 136; Fischer, Beckert, Hafner, and Stahl, *Z. Naturforsch.*, 1955, **10**b, 598.

The product of this reaction has now been isolated as the potassium salt by electrolytic reduction of an aqueous solution of the chromium(I) complex. The product forms blue crystals and is very sensitive to aerial oxidation, which causes reconversion into $[\text{Cr}^{\text{I}}(\text{CN})_5\text{NO}]^{3-}$. The paramagnetism of the complex ($\chi_g = 0{\cdot}22 \times 10^{-6}$ c.g.s.u.) is considerably less than that required for a single unpaired electron; it may arise from a temperature-independent paramagnetic effect or from a small amount of chromium(III) oxidation product. This low paramagnetism indicates that the complex contains chromium(0) and that it is isoelectronic with chromium carbonyl and the recently reported $[\text{Cr}^{0}(\text{CN})_6]^{6-}$ ion.[6] A strong peak at 1515 cm.$^{-1}$ is assigned to the N–O stretching frequency; although this is somewhat low for the stretching mode of a co-ordinated nitrosonium group,[7] a low frequency is also observed for the analogous complex $[\text{V}^{-\text{I}}(\text{CN})_5\text{NO}]^{5-}$ [8] Low N–O and C–N stretching frequencies are to be expected for nitrosyl–cyanide complexes in which the central metal atom has a low effective electronegativity,[8] since in such cases there will be a greater metal–carbon and metal–nitrogen bond multiplicity than there would be if the metal atom were to have a high electronegativity. Thus, in the complexes $[\text{Cr}^{0}(\text{CN})_5\text{NO}]^{4-}$ and $[\text{Cr}^{\text{I}}(\text{CN})_5\text{NO}]^{3-}$ (see Table 1) there is an increase in the frequencies of both the N–O and the C–N stretching vibrations in the latter case.

2. *Pentamminenitrosylchromium*(I) *dichloride*, $[\text{Cr}^{\text{I}}(\text{NO})(\text{NH}_3)_5]\text{Cl}_2$. This new compound was prepared by treating a suspension of chromous chloride in liquid ammonia with nitric oxide. The yellow complex is stable to air and is slowly hydrolysed in aqueous solution. With cyanide ion it yields the pentacyanonitrosylchromate(I) ion, $[\text{Cr}^{\text{I}}(\text{CN})_5\text{NO}]^{3-}$. The magnetic moment of 2·3 B.M. indicates that the chromium is in the (+I) spin-paired state; this is confirmed by the infrared spectrum of the complex (Table 1) which has a peak at 1670 cm.$^{-1}$ that is assigned to the N–O stretching mode arising from a co-ordinated nitrosonium group. Polarographic reduction of an aqueous solution of the complex in 0·1M-potassium chloride shows that it behaves differently from other chromium(III) ammines; there is no reduction before −1·5 v (*vs.* S.C.E.) after which a complicated series of cathodic curves arise, probably associated with reduction of the nitrosyl group.

TABLE 1.

Infrared spectra of chromium and molybdenum complexes.

Complex	NO	CN	Other frequencies
$\text{K}_4[\text{Cr}^{0}(\text{CN})_5\text{NO}],2\text{H}_2\text{O}$	1515vs	2020vs	1630(HOH), 1080, 1043m
$\text{K}_3[\text{Cr}^{\text{I}}(\text{CN})_5\text{NO}],\text{H}_2\text{O}$	1645vs	2137vs, 2095sh, 2170vs, 2125s	
$[\text{Cr}^{\text{I}}(\text{NO})(\text{NH}_3)_5]\text{Cl}_2$	1670vs		1609s, 1290sh, 1273s, 1240sh, 1080w, 1045s, 875w, 770b (all NH_3)
$[\text{Cr}^{\text{I}}(\text{NO})(\text{H}_2\text{O})_5]\text{Cl}_2$	1747vs		1630vs, b (HOH)
$[\text{Cr}^{\text{I}}(\text{NO})(\text{MeOH})_5]\text{Cl}_2$ *	1719vs		
$[\text{Cr}^{\text{I}}(\text{NO})(\text{EtOH})_5]\text{Cl}_2$ †	1718vs		
$\text{K}_4[\text{Mo}^{\text{II}}(\text{CN})_5(\text{OH})_2\text{NO}]$ ‡	1595vs	2130s, 2106s, 2081s, 2062s, 2037s	980m, 835b
$\text{K}_4[\text{Mo}^{\text{IV}}(\text{CN})_5\text{O}_2(\text{NO})],3\text{H}_2\text{O}$	1580vs	2167w, 2125vs, 2040m, b	1640b (HOH), 890vs. 835m (Mo=O)

Frequencies in cm.$^{-1}$. Spectra taken in mulls except * and †, methanol and ethanol solutions, respectively. ‡ Griffith, Lewis, and Wilkinson, *J.*, 1959, 872.

This complex is formally analogous to the pentamminenitrosylcobalt chloride, $[\text{Co}^{\text{III}}(\text{NO})(\text{NH}_3)_5]\text{Cl}_2$ which, however, is diamagnetic and may contain the NO^- ion.[9] It has been shown[10] that $[\text{Cr}^{\text{II}}(\text{NH}_3)_6]^{2+}$ is spin-free, so that the substitution of nitric oxide (which is a strong-field ligand) for an ammonia group is sufficient to cause spin-pairing in the chromium atom.

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[6] Heintz, *J. Inorg. Nuclear Chem.*, 1961, **21**, 262.

[7] Lewis, Irving, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1957, **7**, 32.

[8] Griffith, Lewis, and Wilkinson, *J.*, 1959, 1632.

[9] Griffith, Lewis, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1957, **7**. 38.

[10] Hume and Stone, *J. Amer. Chem. Soc.*, 1941, **63**, 1200.

3. *Chromium*(I) *nitrosyl penta-alcoholate and penta-aquo-ions*, $[Cr^{I}(NO)(ROH)_5]^{2+}$. The penta-aquo-complex was first reported by Ardon and Herman.[3] They considered, on the basis of titrimetric evidence, that the complex contained chromium(III) surrounded by five water ligands and the NO^- group. The red complexes reported by Chesneau [11] and Kohlschutter [12] are probably impure forms of this complex.

The penta-methanolate and -ethanolate complexes were prepared by passing nitric oxide into alcoholic solutions of chromous chloride. Owing to the instability of the complexes, no magnetic measurements were made and the solid compounds could not be isolated. The infrared spectra, however, have peaks near 1720 cm.$^{-1}$ which probably arise from co-ordinated NO^+ groups, so the most likely formulation is $[Cr^{I}(NO)(ROH)_5]^{2+}$.

Although solid salts of the penta-aquo-ion can be isolated,[3] it is difficult to prepare them free from the chromium(III) hexa-aquo-ion and from other penta-aquated species. (A similar difficulty arises when attempts are made to isolate aquo-nitrosyl complexes of iron.) It was found that solutions of the perchlorate were far more stable than those of the chloride or sulphate, presumably because in the last two cases there is a tendency for one or more anionic groups to enter the first co-ordination sphere at the expense of the nitrosyl group. It was decided therefore to check the apparent stoicheiometry, $[Cr(NO)(H_2O)_5]^{2+}$, by spectrophotometric titration with chromous perchlorate solution of various simple and complex ions. For the reactions $NO_x^- + nCr^{2+} \longrightarrow Cr(NO)^{2+}$, the Cr : ion ratios for the series of reactant ions NO_3^-, NO_2^-, $[Co(NH_3)_5ONO]^{2+}$, $[Co(NH_3)_5NO_2]^{2+}$, and $[Co(NH_3)_5NO]^{2+}$ were, respectively, 5 : 1, 3 : 1, 3 : 1, 3 : 1, and 1 : 1 {a result of approximately 4 : 1 was obtained for reaction of $[Co(NH_3)_5NO_3]^{2+}$ with chromous ion, but this salt, as the perchlorate, could not be obtained free from $[Co(NH_3)_5H_2O]^{3+}$}. It is clear from these results that in each case the ion has been reduced and that the ratio of chromium to nitric oxide in the complex is 1 : 1, in agreement with the reported formulation.[3] Reaction between chromous ion and the pentamminecobalt(III) ions appeared to be somewhat faster than that between chromous and the aquo-pentammine-ion of cobalt(III).

In most cases, the reaction $[Co^{III}(NH_3)_5X]^{2+} + [Cr^{II}(H_2O)_6]^{2+} = Co^{2+} + [Cr^{III}(H_2O)_5X]^{2+}$ follows a ligand-bridged path, the ligand X being transferred unchanged to the chromium atom.[13,14] In these reactions, however, it appears that the ligand is reduced by the chromous ion to NO^+ which is then co-ordinated to chromium(II).

On the basis of the fact that the complex reacts with four equivalents of ceric ion, Ardon and Herman [3] concluded that the chromium was in the (+3) state and the nitrogen in the (+1) state, so that the complex would contain a NO^- group co-ordinated to chromium(III) (a similar structure has been postulated for the red series of cobalt nitroso-pentammines [9]). However, since both the formally analogous chromium nitrosyl cyanide and nitrosyl ammines contain chromium(I), this structure seems somewhat unlikely.

Magnetic-susceptibility measurements of aqueous solutions of the complex (Table 2) indicate the presence of a single unpaired electron per chromium atom, and infrared spectra show strong absorption at 1747 cm.$^{-1}$, indicating the presence of a co-ordinated NO^+ group. If the structure were $[Cr^{III}(NO)(H_2O)_5]^{2+}$ with NO^-, the magnetic moment would correspond to that required for three unpaired electrons, and the N–O stretching frequency would, on the basis of results observed for the cobalt nitroso-pentammines,[9,15] lie near 1150 cm.$^{-1}$. It therefore seems more likely that the correct formulation is $[Cr^{I}(NO)(H_2O)_5]^{2+}$, analogous to the " brown-ring " salts of iron, $[Fe^{I}(NO)(H_2O)_5]^{2+}$,[16] but differing from the latter in that the chromium(I) is spin-paired, as shown by the low

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[11] Chesneau, *Compt. rend.*, 1899, **129**, 100.

[12] Kohlschutter, *Ber.*, 1904, **37**, 3053.

[13] Norman, Taube, and Posey, *J. Amer. Chem. Soc.*, 1957, **79**, 262.

[14] Taube, Ball, and King, *J. Amer. Chem. Soc.*, 1958, **80**, 1091; Taube, *Canad. J. Chem.*, 1959, **37**, 129.

[15] Griffith, Lewis, and Wilkinson, *J.*, 1961, 775.

[16] Griffith, Lewis and Wilkinson, *J.*, 1958, 3993.

TABLE 2.

Magnetic measurements on chromium and molybdenum complexes.

Complex	χ_g	χ_a	$\mu_{eff.}$	Temp. (K)
$K_4[Cr(CN)_5NO],2H_2O$	0·22	220	0·7	295°
$K_3[Cr(CN)_5NO],H_2O$	3·7	1440	1·87	297
$[Cr(NO)(NH_3)_5]Cl_2,H_2O$	8·75	2239	2·3	295
$[Cr(NO)(H_2O)_5](ClO_4)_2$ *	3·83	1990	2·2	295
$K_4[Mo(CN)_5NO(OH)_2]$	0·36	330	0·9	295
$K_4[Mo(CN)_5NO(O_2)],3H_2O$	0	170	0·6	295

* Measured in aqueous solution by the nuclear magnetic resonance method; others by the Gouy method on solid samples. Susceptibilities in c.g.s.u. × 10^6; moments in Bohr magnetons.

magnetic moment. {It may be noted here that the titrimetric results of Ardon and Herman will not distinguish between $[Cr^{III}(NO)(H_2O)_5]^{2+}$ with chromium(III) and $N^{I}O^{-}$, and $[Cr^{I}(NO)(H_2O)_5]^{2+}$ with chromium(I) and $N^{III}O^{+}$}. The penta-aquo-complex reacts with cyanide ion to give an ion $[Cr^{I}(CN)_5NO]^{3-}$.

TABLE 3.

Absorption spectra of chromium and molybdenum nitrosyl complexes in aqueous solutions.

Complex	λ (mμ)	ε	λ	ε	λ	ε	λ	ε
$K_3[Cr(CN)_5NO]$	724	14·5	447	127	335sh	86	270sh	2448
$[Cr(NO)(H_2O)_5](ClO_4)_2$	567	30·6	447	131	390sh	96	324	101
$[Cr(NO)(C_2H_5OH)_5]Cl_2$	570	18	457	61	325	150		
$[Cr(NO)(NH_3)_5]Cl_2$	457	101	348	69	302	157	257	1460
$K_4[Mo(CN)_5(NO)(O)_2]$	383	45	327	65	297	187		

(B) *Molybdenum Nitrosyl Complexes.*—Apart from a cyclopentadienyl carbonyl nitrosyl, $CpMo(NO)(CO)_2$,[5] the only known nitrosyl complex of molybdenum is the eight co-ordinated $K_4[Mo^{II}(CN)_5(NO)(OH)_2]$.[2,17,18]

Potassium pentacyanonitrosyldioxomolybdate(IV), $K_4[Mo^{IV}(CN)_5(NO)O_2]$. If the nitrosylpentacyano-complex of molybdenum(II) is exposed to the atmosphere, or if air or oxygen is passed into an aqueous or alkaline solution of $[Mo^{II}(CN)_5NO(OH)_2]^{4-}$, this new complex is formed.

It is very stable, both in the solid state and in aqueous solution, and it has the yellow colour of many molybdenum(IV) cyano-complexes. It is diamagnetic in the solid state and in solution, and its infrared spectrum (Table 1) has a peak at 1580 cm.$^{-1}$ which may be attributed to co-ordinated NO^+. Electrolytic reduction of an aqueous solution of the complex at a mercury cathode regenerates the purple molybdenum(II) complex.

The infrared spectrum of the complex deserves comment. There are no peaks which may be attributed to the $-NO_2$ or $-NO_3$ groups; the splitting of the C–N stretching frequency bands in the 2000—2150 cm.$^{-1}$ regions is far less complex than is the case for $[Mo^{II}(CN)_5(NO)(OH)_2]^{4-}$. There are very intense bands at 890 and 835 cm.$^{-1}$ which may be attributed to Mo=O stretching vibrations.[2,19] The most remarkable feature, however, is that neither the N–O nor C–N stretching frequencies increase in frequency: in general, N–O and C–N stretching vibrations increase as the oxidation state of the central metal atom increases, for reasons already suggested. In this case it seems possible that this is associated with the unusual stereochemistry of the complex and the presence of Mo=O groups; the electronegativity of O^{2-} is substantially lower than that of OH^-, and this may counterbalance the larger electronegativity of molybdenum(IV) over molybdenum(II); If the electronegativity of the molybdenum remains approximately the same for the two cases, little change in the C–N and N–O bond multiplicities would be expected.

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[17] Van der Steide and Hofmann, *Z. anorg. Chem.*, 1896, **12**, 282.
[18] Nast and Gehring, *Z. anorg. Chem.*, 1948, **256**, 169.
[19] Barraclough, Lewis, and Nyholm, *J.*, 1959, 3552.

EXPERIMENTAL

Potassium Nitrosylpentacyanochromate(0), $K_4[Cr^0(CN)_5NO],2H_2O$. A 0·1M-solution of $K_3[Cr(CN)_5NO],H_2O$ in 0·1M-potassium cyanide and 0·1M-potassium hydroxide was electrolytically reduced, a mercury cathode and a platinum anode being used. The blue solution was filtered under nitrogen and the filtrate added to air-free anhydrous ethanol. The blue *complex* that was precipitated was filtered off and washed (in a nitrogen atmosphere) with 95% ethanol, anhydrous methanol, and ether, and was dried *in vacuo* (Found: K, 39·0; Cr, 12·5; N, 20·1; H, 1·0. $H_4C_5CrK_4N_6O_3$ requires K, 38·8; Cr, 12·9; N, 20·8; H, 1·0%).

Pentamminenitrosylchromium(I) *Dichloride*, $[Cr^I(NO)(NH_3)_5]Cl_2,H_2O$.—Anhydrous liquid ammonia (50 ml.) was added to anhydrous chromous chloride (5 g.), and dry nitric oxide (free from nitrogen dioxide) was passed through the suspension for an hour. The remaining liquid was poured off and the yellow precipitate of *complex* was washed with liquid ammonia, dried, washed with ice-cold water, alcohol, and ether, and dried *in vacuo* (Found: Cr, 20·2; N, 32·2; Cl, 28·6. $H_{17}CrCl_2N_6O_2$ requires Cr, 20·3; N, 32·8; Cl, 27·8%).

Penta-aquonitrosylchromium(I) *Dichloride*, $[Cr^I(NO)(H_2O)_5]Cl_2$.—A 0·05M-solution of chromic chloride in 0·05M-perchloric acid was electrolytically reduced, with a platinum anode and mercury cathode. The resulting blue solution of chromous chloride was added dropwise to a flask through which a rapid stream of nitrogen dioxide-free nitric oxide was passing. The resulting deep-red solution was passed down a Dowex-50 cation-exchange column (50—100 mesh),[3,20] and the nitrosyl complex was eluted with 0·7M-hydrochloric acid (similar methods, with the appropriate acids, were used to obtain solutions of the sulphate and perchlorate). The solid chloride, mixed with some of the salts $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]Cl_2$, was then obtained by evaporating the aqueous solution over phosphorus pentoxide.

Nitrosylpentamethanol- and -pentaethanol-chromium(I) *Dichloride*, $[Cr^I(NO)(ROH)_5]Cl_2$.—These were prepared in solution by passing anhydrous, nitrogen dioxide-free nitric oxide into methanolic and ethanolic solutions of chromous chloride. The solutions slowly decompose in air to nitric oxide and chromic ion; they are slowly decomposed by addition of water.

Potassium Pentacyanonitrosylchromate(I), $K_3(Cr(CN)_5NO],H_2O$.—This was made by the method of Griffith, Lewis, and Wilkinson [15] (Found: K, 33·6; Cr, 14·9; C, 18·05; N, 24·3; H_2O, 5·1. Calc. for $H_2C_5CrK_3N_6O_2$: K, 33·8; Cr, 15·0; C, 17·3; N, 24·2; H_2O, 5·2%).

Potassium Pentacyanonitrosylchromate(I) *from* $[Cr(NO)(H_2O)_5](ClO_4)_2$.—The perchlorate was made in solution as described above and added to an excess of potassium cyanide solution. The solution was filtered and added to alcohol. The green precipitate of *complex* was filtered off and washed with alcohol and ether (Found: C, 17·0; N, 24·0. $H_2C_5CrK_3N_6O_2$ requires C, 17·3; N, 24·2%).

Potassium Dihydroxypentacyanonitrosylmolybdate(II), $K_4[Mo^{II}(CN)_5(OH)_2NO]$.—This was prepared by Nast's method [18] (Found: K, 35·5; C, 13·1. Calc. for $H_2C_5K_4MoN_6O_3$ requires K, 34·9; C, 13·5%).

Potassium Dioxypentacyanonitrosylmolybdate(IV), $K_4[Mo^{IV}(CN)_5(NO)O_2],3H_2O$.—This *molybdate* was prepared by exposing the salt $K_4[Mo^{II}(CN)_5(NO)(OH)_2]$to the atmosphere for 48 hr., until the purple colour had quite disappeared. The yellow salt was then dissolved in the minimum quantity of water and, after filtration, re-precipitated with alcohol, filtered off, and washed with alcohol and ether; the procedure was repeated (Found: K, 31·8; C, 12·8; N, 17·4. $H_6C_5K_4MoN_6O_6$ requires K, 32·4; C, 12·5; N, 17·4%).

Nitritopentamminecobalt(III) *Perchlorate*, $[Co^{III}(NH_3)_5ONO](ClO_4)_2$.—This was prepared by the method of Linhard *et al.*[21] (Found: Co, 14·5; N, 21·8. Calc. for $H_{15}Cl_2CoN_6O_{10}$: Co, 15·2; N, 21·6%).

Nitropentamminecobalt(III) *Perchlorate*, $[Co^{III}(NH_3)_5NO_2](ClO_4)_2$.—This was made by warming a solution of the nitritopentammine to 50° until isomerisation was complete, and recrystallising the *product* from water (Found: Co, 14·8; N, 21·2; ClO_4^-, 52·0. Calc. for $H_{15}Cl_2CoN_6O_{10}$: Co, 15·2; N, 21·6; ClO_4^-, 51·1%).

Pentamminenitrosylcobalt(III) *Perchlorate*, $[Co^{III}(NH_3)_5NO](ClO_4)_2,3H_2O$.—This *salt* was prepared by treating a suspension of hexamminecobalt(II) perchlorate in aqueous ammonia

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[20] Gustavson, *Svensk kem. Tidskr.*, 1944, **56**, 14; King and Dismukes, *J. Amer. Chem. Soc.*, 1952, **74**, 1674; King, Woods, and Gates, *ibid.*, 1958, **80**, 5015.

[21] Linhard, Siebert, and Weigel, *Z. anorg. Chem.*, 1955, **278**, 287.

with nitric oxide gas for an hour (Found: N, 19·9; Cl, 16·3. $H_{15}Cl_2CoN_6O_8$ requires N, 19·7; Cl, 16·6%).

General.—Spectrophotometric titrations with chromous ion and complex ions to give $[CrNO(H_2O)_5]^{2+}$ were performed by observing the decrease and eventual disappearance of the cobalt(III) bands in the optical range, and in the case of simple ions (NO_3^-, NO_2^-) with chromous ion by observing the growth of the $[CrNO(H_2O)_5]^{2+}$ bands at 324 and 447 mμ. Under these conditions the reactions appear to be stoicheiometric.

Infrared spectra were measured on a Perkin-Elmer Model 21 recording spectrophotometer with sodium chloride optics; visible and ultraviolet absorption spectra on a Carey recording spectrophotometer with quartz 1-cm. cells; polarograms on a Sargent model XV recording instrument; susceptibility measurements by the nuclear magnetic resonance method on a Varian 40 Mc./sec. instrument, with 3% t-butyl alcohol–water solution.[22] Chromium was analysed spectrophotometrically as chromate, potassium gravimetrically as the tetraphenylborate; carbon, hydrogen, nitrogen, and chlorine analyses were performed by the Mikroanalytisches Laboratorium im Max-Planck Institut für Kohlenforschung, Mülheim.

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[22] Evans, *J.*, 1959, 2003.