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Telluroamides and Selenoamides: Complexes with Chromium, Molybdenum, and Tungsten Pentacarbonyls

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ABSTRACT

*Several new telluroamide and selenoamide group 6 metal complexes (***2a–2f***), C_5H_9NOE-$M(CO)_5$, where E is Te or Se and M is Cr, Mo, or W, have been successfully synthesized by the reaction between PyM$(CO)_5$ and 4-(telluroformyl)morpholine (***1a***) or 4-(selenoformyl)morpholine (***1b***). The crystal structures of C_5H_9NOSe (***1b***), C_5H_9NOTe-$Cr(CO)_5$ (***2a***), and C_5H_9NOSe-$Cr(CO)_5$ (***2d***) have been determined. The changes in the physical properties and structures between free ligands (***1a, 1b***) and coordinated telluro- or selenocarbonyls (in complexes* **2a–2f***) have been investigated.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem **9**:57–64, 1998

INTRODUCTION

The coordination chemistry of selenium and tellurium ligands has been actively studied and excellently reviewed [1–6]. However, the tellurium ligands that have been studied are limited almost entirely to inorganic polytellurides (Te_n^{2-}, $n = 2$–6) or organic tellurides (R_2Te). Tellurocarbonyls that are of great potential interest with respect to their structures, properties, and reactions represent a completely different type of tellurium ligand. Due to the difficulty in their preparation, the ligand properties of tellurocarbonyls have not been well explored. A few metal complexes in which telluroaldehydes [7–12], telluroketones [13–15], and telluroureas [16,17] function as ligands have been reported. To date, however, no example in which a telluroamide functions as a ligand has appeared in the literature. Recently, we have described the successful syntheses and crystal structures of two telluroamides [18]. The availability of these compounds has enabled us to investigate some new telluroamide-metal complexes. We report here the syntheses and structures of 4-(telluroformyl)morpholine complexes of group 6 metal pentacarbonyls and their selenium analogs, C_5H_9NOE-$M(CO)_5$, where E is Te or Se and M is Cr, Mo, or W. Also, comparisons are made between the physical properties of the complexes and the free molecules.

EXPERIMENTAL

General

THF was refluxed over potassium and distilled under argon prior to use. Selenium and tellurium powders were furnished by Phelps Dodge and NORANDA, Inc. Hexacarbonyls, $M(CO)_6$ (M: Cr, Mo, W), were obtained from Strem Chemicals, Inc. All other laboratory reagents were purchased from Aldrich Chemical Co. 4-(Telluroformyl)morpholine (**1a**) was prepared as previously described [18]. The prepara-

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Dedicated to Prof. William E. McEwen on the occasion of his seventy-fifth birthday.

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tion of 4-(selenoformyl)morpholine (**1b**) is described in the Experimental section.

^{1}H and ^{13}C NMR spectra were run on a Varian XL-200 NMR spectrometer (200.1 MHz for ^{1}H, 50.3 MHz for ^{13}C). ^{77}Se and ^{125}Te NMR spectra were measured on a Varian XL-200 broadband NMR spectrometer (38.2 MHz for ^{77}Se, 63.1 MHz for ^{125}Te) with PhSeSePh (δ 460 referenced to Me_2Se) [19] or PhTeTePh (δ 420.8 referenced to Me_2Te) [20] as the external standards. $CDCl_3$ was used as the solvent in the NMR measurements for the selenium compounds, while C_6D_6 was used for dissolution of the tellurium compounds (because they are more stable in C_6D_6 than in $CDCl_3$). ^{1}H NMR chemical shifts were referenced to the residual proton line (δ 7.24) from $CDCl_3$ (99.8% D) and ^{13}C NMR chemical shifts to $CDCl_3$ (δ 77). ^{77}Se/^{125}Te NMR chemical shifts were converted relative to Me_2Se or Me_2Te. IR spectra were recorded on an IBM IR/32 using a CaF_2 cell (0.1 mm). Mass spectra were run using a VG-70S spectrometer in the +FAB/DP mode. Melting points were determined on a Fisher–Johns melting-point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc.

Preparation of Metal Pyridine Pentacarbonyls

PyM(CO)$_5$, M is Cr, Mo, or W. A mixture of 5.0 g of the hexacarbonyl, $M(CO)_6$ (M: Cr, Mo, W) and pyridine (5.0 mL) was refluxed in xylene (50 mL) for 2.0 hours. The solvent was evaporated and the residue was separated by column chromatography on Silica gel (60–200 mesh) with hexane and then hexane-CH_2Cl_2 as the solvents. Evaporation of the eluate gave $PyM(CO)_5$. Each was identified by comparison with the respective spectroscopic data (^{1}H, ^{13}C NMR) and melting points as reported in the literature [21–24]. Identification of $PyCr(CO)_5$ was confirmed by mass spectrometry.

PyCr(CO)$_5$. Yellow-brown solid, mp 92.0–94.0°C, yield 2.72 g (43.6%). ^{1}H NMR ($CDCl_3$, δ): 8.57 (d, br, 2H), 7.70 (t, br, 1H), 7.22 (t, br, 2H). ^{13}C NMR ($CDCl_3$, δ): 220.73 (*trans*-CO), 214.37 (*cis*-CO), 155.38, 137.17, 124.88. Mass (EI; *m/e*): 271 (M^+), 243 ($[M\text{-}CO]^+$), 159 ($[M\text{-}4CO]^+$), 131 ($[M\text{-}5CO]^+$).

PyMo(CO)$_5$. Brown solid, mp 83.0–85.0°C, yield 2.10 g (36%). ^{1}H NMR ($CDCl_3$, δ): 8.53–8.60 (m, 2H), 7.60–7.80 (m, 1H), 7.15–7.30 (m, 2H). ^{13}C NMR ($CDCl_3$, δ): 214.05 (*trans*-CO), 204.30 (*cis*-CO), 154.77, 137.40, 124.96.

PyW(CO)$_5$. Yellow solid, mp 105.0–106.0°C, yield 2.64 g (46.8%). ^{1}H NMR ($CDCl_3$, δ): 8.76 (d, br, 2H), 7.74 (t, br, 1H), 7.23 (t, br, 2H). ^{13}C NMR ($CDCl_3$, δ): 202.31 (*trans*-CO), 198.84 (*cis*-CO), 156.00, 137.37, 125.62.

Preparation of 4-(Selenoformyl)morpholine

C_5H_9NOSe (1b). The procedure reported by Segi and co-workers [25] was used. 4-(Selenoformyl)morpholine, C_5H_9NOSe (480 mg, 82.7%), was obtained in the form of a yellow solid (mp 77.0–78.0°C) from the reaction between 4-formylmorpholine (400 mg, 3.44 mmol) and $Me_2AlSeAlMe_2$. The latter was generated in situ via the Sn–Al transmetallation reaction between $Bu_3SnSeSnBu_3$ (2.15 g, 3.26 mmol) and Me_3Al (2 M toluene solution, 3.50 mL, 7.0 mmol). Anal. calcd for C_5H_9NOSe (FW 178.09): C, 33.72; H, 5.09; N, 7.86. Found: C, 33.69; H, 4.75; N, 7.87. Spectral data are shown in Table 2.

General Procedure for Preparation of 4-(Telluroformyl)morpholine Complexes

C_5H_9NOTe-$M(CO)_5$ (**2a**: *M = Cr;* **2b**: *M = Mo;* **2c**: *M = W*). Under an atmosphere of dry argon, a mixture of 4-(telluroformyl)morpholine (250 mg, 1.103 mmol) and $PyM(CO)_5$ (1.325 mmol, 1.2 equiv) in dry THF (15 mL) was heated in an aluminum-foil-wrapped 50 mL three-necked flask at 50–60°C for 1.0 hour. Following evaporation of the reaction mixture, the complexes were isolated by column chromatography on Florisil (60–100 mesh) using benzene as the eluting solvent. All data are given in Tables 1 and 2.

General Procedure for Preparation of 4-(Selenoformyl)morpholine Complexes

C_5H_9NOSe-$M(CO)_5$ (**2d**: *M = Cr;* **2e**: *M = Mo;* **2f**: *M = W*). A mixture of 4-(selenoformyl)morpholine (200 mg, 1.123 mmol) and $PyM(CO)_5$ (1.143 mmol, 1.1 equiv) in dry THF (15 mL) was refluxed for 2.0 hours under an argon atmosphere. After evaporation, the reaction mixture was chromatographed through Silica gel (60–200 mesh) using hexane and then hexane-CH_2Cl_2 (2:1 → 1:1) as the solvent. Evaporation of the eluate gave the respective complexes. All data are listed in Tables 1 and 2.

X-ray Structure Determination

Crystals of **2a** for X-ray analysis were prepared by recrystallization from hexane–benzene (2:1) at −15°C. X-ray-quality crystals of **1b** and **2d** were obtained from solutions in CH_2Cl_2 stored under refrig-

TABLE 1 Physical Data of Compounds **2a**–**2f**

					Elemental Analysis: Calcd (Found), %		
Compd.	*Form*	*Mp (°C)*	*Yield (%)*	*Molecular Formula*	*C*	*H*	*N*
2a	dark-red solid	66.0 (dec.)	65	$C_{10}H_9NO_6CrTe$ (418.78)	28.68 (19.71)[a]	2.17 (2.65)	3.34 (3.16)
2b	black solid	70.0 (dec.)	58.8	$C_{10}H_9NO_6MoTe$ (462.72)			
2c	dark-red solid	76.0 (dec.)	68	$C_{10}H_9NO_6WTe$ (550.63)			
2d	yellow crystal	96.0–97.0	62.5	$C_{10}H_9NO_6CrSe$ (370.14)	32.45 (31.57)	2.45 (2.59)	3.78 (3.68)
2e	black solid	100.0–102.0	41	$C_{10}H_9NO_6MoSe$ (414.09)	29.01 (28.73)	2.19 (2.42)	3.38 (3.42)
2f	greenish-brown solid	108.0–110.0	71	$C_{10}H_9NO_6WSe$ (502.00)	23.93 (23.50)	1.81 (1.92)	2.79 (2.78)

[a] The sample decomposed during the delivery. Also for this reason, compounds **2b** and **2c** were not subjected to elemental analysis.

eration. A yellow needle crystal of **1b**, an orange block of **2a**, and a yellow block of **2d** were mounted on glass fibers at room temperature. Preliminary examination and data collection were performed on a Siemens R3M (oriented graphite monochrometer; Mo $K\alpha$ radiation) at 293 (2) K for **1b** and **2d**, a Siemens P4 (oriented graphite monochrometer; Mo $K\alpha$ radiation) at 193 (2) K for **2a**. Cell parameters for all three structures were calculated from the least-squares fitting for 25 high-angle reflections ($2\theta > 15°$). ω scans for several intense reflections indicated acceptable crystal quality. For **1b**, **2a**, and **2d**, data was collected from 4° to 50° 2θ, and scan width for data collection was 1° in ω with a variable scan rate between 2° and 15°/min. The three standards, collected every 97 reflections for **1b**, **2a**, and **2d**, showed no significant trends. Background measurement by stationary crystal and stationary counter technique at the beginning and the end of each scan for 1/2 the total scan time.

Lorentz and polarization corrections were applied to 1367 reflections for **1b**, 2595 reflections for **2a**, and 2630 reflections for **2d**. A semiempirical absorption correction was applied. A total of 896 unique observed reflections ($R_{\text{int}} = 0.053$) for **1b**, 2302 reflections ($R_{\text{int}} = 0.027$) for **2a**, and 1767 reflections ($R_{\text{int}} = 0.0387$) for **2d** were used in the calculation of R(F). All three structures were solved by direct methods [26] and refined using a full-matrix least-squares anisotropic refinement for all nonhydrogen atoms [27]. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 1.5 times the parameter of the attached atom. Neutral atom-scattering factors and anomalous scattering factors were taken from the *International Table for X-ray Crystallography,* Vol. C. Crystal structure parameters are listed in Table 3, and the atomic coordinates and isotropic thermal parameters for nonhydrogen atoms are given in the Supporting Information.

RESULTS AND DISCUSSION

Syntheses

4-(Telluroformyl)morpholine (**1a**) and 4-(selenoformyl)morpholine (**1b**) were prepared according to published procedures [18,25]. $PyM(CO)_5$, where M is Cr, Mo, and W, were easily prepared by the reaction between the respective hexacarbonyls and pyridine in refluxing xylene. **1a** or **1b** undergo reaction with $PyM(CO)_5$ to afford the corresponding complexes **2a–2f**, $C_5H_9NOE\text{-}M(CO)_5$, where E is Te or Se and M is Cr, Mo, or W (Scheme 1). Selenium complexes **2d–2f** were obtained as stable compounds. However, tellurium compounds **2a–2c**, like the free ligand **1a**, were very unstable. They decomposed quickly on standing, even at refrigerator temperature. It is well known that telluroaldehydes and telluroketones can be stabilized by coordination to transition metals such as Cr, Mo, and W [28]. The present observations show that coordination to these metals does not stabilize telluroamides. This suggests that the bond between telluroamides and group 6 metals (Cr, Mo, and W) is weak. This conclusion is supported by the data obtained from X-ray crystallographic studies.

Spectroscopic Properties

The spectral data of complexes **2a–2f** and the free molecules **1a–1b** are summarized in Table 2. Similar to other $LM(CO)_5$-type compounds [29–31], all these complexes (**2a–2f**) have C_{4v} symmetry of the $M(CO)_5$

TABLE 2 Spectral Data of Compounds **1a–1b** and **2a–2f**

	NMR (δ)[a]			IR (cm^{-1})[b]	Mass
Compd.	^1H	^{13}C	$^{77}Se/^{125}Te$	ν (CO)	(+FAB/DP; m/e)
1a	12.54 (s, 1H, NC**H**Te) 3.63 (t, J = 5.0 Hz, 2H) 3.07 (t, J = 5.0 Hz, 2H) 2.73 (t, J = 4.9 Hz, 2H) 2.20 (t, J = 4.9 Hz, 2H)	179.55 (N**C**HTe) 65.81, 65.29, 60.12, 54.46	888.2		
1b	10.68 (s, 1H, NC**H**Se) 4.14 (t, br, 2H) 3.73–3.82 (m, 4H) 3.62 (t, br, 2H)	189.62 (N**C**HSe) 66.60, 65.84 57.79, 48.87	544.9		180 ([M+H]$^+$, ^{80}Se)
2a	11.25 (s, 1H, NC**H**Te) 2.76 (s, br, 4H) 2.50 (t, J = 4.8 Hz, 2H) 1.77 (t, J = 4.8 Hz, 2H)	224.50 (*trans*-CO) 218.58 (*cis*-CO) 178.40 (N**C**HTe) 66.31, 65.50 61.43, 56.03	154.6	2050.6 (m), A_1 1972.5 (w), B_1 1931.0 (vs), E 1904.2 (s), A_1	421 (M$^+$, ^{130}Te)
2b	11.38 (s, 1H, NC**H**Te) 2.77–2.98 (d, br, 4H) 2.58 (s, br, 2H) 1.90 (s, br, 2H)	213.00 (*trans*-CO) 207.56 (*cis*-CO) 176.86 (N**C**HTe) 65.63, 64.73 60.24, 54.83	154.6	2062.2 (s), A_1 1975.0 (w), B_1 1934.9 (vs), E 1902.1 (s), A_1	465 (M$^+$, ^{130}Te)
2c	11.36 (s, 1H, NC**H**Te) 2.75 (s, 4H) 2.49 (t, J = 4.8 Hz, 2H) 1.78 (t, J = 4.8 Hz, 2H)	213.50 (*trans*-CO) 198.19 (*cis*-CO) 179.93 (N**C**HTe) 66.35, 65.49 61.39, 55.37	155.6	2062.2 (s), A_1 1966.0 (s), B_1 1921.1 (vs), E 1904.2 (sh), A_1	553 (M$^+$, ^{130}Te)
2d	10.11 (s, 1H, NC**H**Se) 4.00 (s, br, 2H) 3.84 (s, br, 4H) 3.70 (s, br, 2H)	223.89 (*trans*-CO) 216.96 (*cis*-CO) 190.73 (N**C**HSe) 66.48, 65.55 58.43, 55.40	340.2	2058.3 (s), A_1 1980.0 (w), B_1 1931.0 (vs), E 1900.1 (s), A_1	372 ([M+H]$^+$, ^{80}Se)
2e	10.21 (s, 1H, NC**H**Se) 4.03 (t, br, 2H) 3.84 (m, 4H) 3.69 (t, br, 2H)	213.35 (*trans*-CO) 205.59 (*cis*-CO) 190.82 (N**C**HSe) 66.42, 65.48 58.33, 49.88	318.8	2068.0 (s), A_1 1981.5 (w), B_1 1936.8 (vs), E 1898.2 (s), A_1	416 ([M+H]$^+$, ^{80}Se
2f	10.27 (s, 1H, NC**H**Se) 3.94–4.00 (m, 2H) 3.77–3.85 (m, 4H) 3.64–3.69 (m, 2H)	201.51 (*trans*-CO) 198.21 (*cis*-CO) 192.32 (N**C**HSe) 66.47, 65.48 58.37, 49.95	270.55	2067.6 (m), A_1 1929.1 (vs), E 1895.4 (s), A_1	504 ([M+H]$^+$, ^{80}Se)

[a] Measured in C_6D_6 (for **1a** and **2a–2c**) or in $CDCl_3$ (for **1b** and **2d–2f**); ^{1}H NMR chemical shifts referenced to the residual C_6D_6 (δ 7.15) or $CHCl_3$ (δ 7.24); ^{13}C chemical shifts referenced to C_6D_6 (δ 128) or $CDCl_3$ (δ 77); ^{77}Se/^{125}Te NMR using Ph_2Se_2 or Ph_2Te_2 as the external standards, chemical shifts relative to Me_2Se (δ 0) or Me_2Te (δ 0).

[b] Measured in THF solution using CaF_2 cell (0.1 mm).

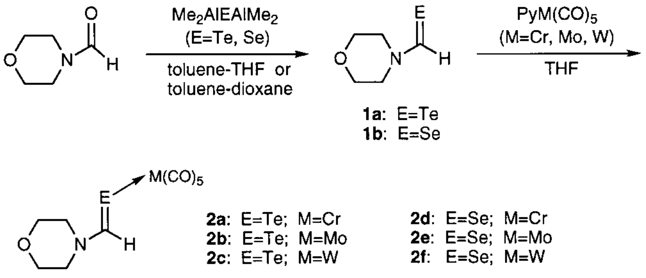
moiety, with the radial CO groups bent slightly out of the plan. Therefore, in their spectra, four carbonyl bands ($2A_1 + E + B_1$) are observed, except for **2f** in which the B_1 band does not appear and only three bands are observed. The assignment of the four bands has been made in comparison with the literature data of similar compounds [29–31] and are shown in Table 2.

The ^{1}H NMR spectra, when compared with that of the free molecule **1a**, show that all protons in complexes **2a–2c** appear at higher fields. However, there is observed only little difference between **1b** and its complexes **2d–2f.** In the cases of **2b** and **2d–2f,** the couplings between the protons on the morpholine ring were broad and difficult to resolve. In the ^{13}C NMR spectra, for all compounds **2a–2f,** the chemical shifts of the C_5H_9NOE portion are changed only within ±2 ppm compared with the same carbons of the free ligands **1a** or **1b.** The *trans*-CO carbons resonate at lower fields than the *cis*-carbonyls. In addition, the chemical shifts of carbonyls (δ CO) have only changed within 3 ppm when the ligand, Py, of $PyM(CO)_5$ is replaced by **1a** or **1b.**

In the ^{77}Se NMR spectra, compounds **2d–2f** res-

TABLE 3 Crystal Data and Structure Refinement for **1b, 2a**, and **2d**

	1b	**2a**	**2d**
Empirical formula	C_5H_9NOSe	$C_{10}H_9CrNO_6Te$	$C_{10}H_9CrNO_6Se$
Formula weight	178.09	418.78	370.14
Temperature/K	293 (2)	193 (2)	293 (2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
Unit cell dimensions			
a/Å, α/°	5.109 (3), 90	10.065 (3), 90	10.215 (2), 90
b/Å, β/°	7.622 (4), 93.74 (5)	11.662 (2), 93.80 (2)	10.529 (2), 118.09 (3)
c/Å, γ/°	17.956 (10), 90	11.893 (3), 90	13.153 (3), 90
V/A^2, Z	697.7 (7), 4	1392.9 (6), 4	1410.8 (5), 4
Density (calculated)	1.695 Mg/m^3	1.997 Mg/m^3	1.743 Mg/m^3
Absorption coefficient	5.289 mm^{-1}	2.839 mm^{-1}	3.409 mm^{-1}
F (000)	352	800	728
Crystal size	0.8 × 0.1 × 0.1 mm	0.9 × 0.4 × 0.4 mm	0.25 × 0.21 × 0.21 mm
θ range for data collection	2.27 to 25.00	2.03 to 25.02	2.48 to 25.03
Limiting indices	$0 \leq h \leq 6$, $0 \leq k \leq 9$, $-21 \leq l \leq 21$	$0 \leq h \leq 11$, $0 \leq k \leq 13$, $-14 \leq l \leq 14$	$-12 \leq h \leq 0$, $-12 \leq k \leq 0$, $-15 \leq l \leq 15$
Reflections collected	1367	2595	2630
Independent reflections	1221 ($R_{int} = 0.0530$)	2449 ($R_{int} = 0.0270$)	2484 ($R_{int} = 0.0387$)
Absorption correction	ψ-scan	semiempirical from ψ-scans	semiempirical from ψ-scans
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
No. of data/restraints/ parameters	1220/0/747	2443/0/173	2483/0/172
Goodness-of-fit on F^2	1.042	1.124	1.025
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0541$, $wR2 = 0.1395$	$R1 = 0.0306$, $wR2 = 0.0815$	$R1 = 0.0471$, $wR2 = 0.0950$
R indices (all data)	$R1 = 0.0776$, $wR2 = 0.1726$	$R1 = 0.0331$, $wR2 = 0.0892$	$R1 = 0.0778$, $wR2 = 0.1111$
Extinction coefficient	0.024 (4)	0.0408 (13)	
Largest diff. peak and hole (eA^{-3})	0.826 and −1.474	0.744 and −1.142	0.523 and −0.338



SCHEME 1

onate at higher fields than the free molecule **1b** ($\delta_{2d} - \delta_{1b} = -204.7$, $\delta_{2e} - \delta_{1b} = -226.1$, $\delta_{2f} - \delta_{1b} = -274.3$ ppm, see Table 2). The ^{125}Te NMR chemical shifts of **2a–2c** are at much more higher fields than that of **1a** ($\delta_{2a} = \delta_{2b} = \delta_{2c} - 1 = \delta_{1a} - 733.6$ ppm, see Table 2), but they remain almost the same among the three complexes. These results suggest that group 6 metals (Cr, Mo, and W) affect a considerable change in the electronic and steric environments of the selenium atom in **1b** or tellurium in **1a.** The different metals show different effects when coordinated to selenium (**1b**), but they have almost the same effect when coordinated to tellurium (**1a**).

Crystal Structures

Only few crystal structures of metal complexes of telluroaldehydes [11], telluroketones [15], and tellureoureas [16] have been reported. In the present investigation, the structural changes between free and coordinated tellurocarbonyls have been studied. In this work, we have determined the crystal structures of 4-(telluroformyl)morpholine pentacarbonyl chromium (**2a**), 4-(selenoformyl)morpholine (**1b**), and 4-(selenoformyl)morpholine pentacarbonyl chromium (**2d**). The structural data of 4-(telluroformyl)morpholine (**1a**) were taken from our previous article [18]. The ORTEP drawings are shown in Figures 1–3, and the selected bond lengths and angles are listed in Tables 4 and 5.

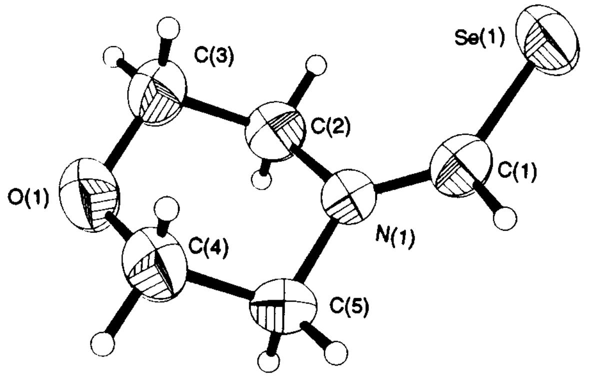


FIGURE 1 ORTEP diagram (50% thermal ellipsoids) of C_5H_9NOSe (1b).

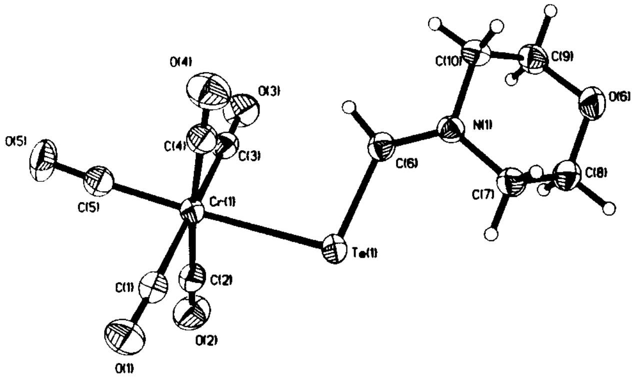


FIGURE 2 ORTEP diagram (50% thermal ellipsoids) of $C_{10}H_9CrNO_6Te$ (2a).

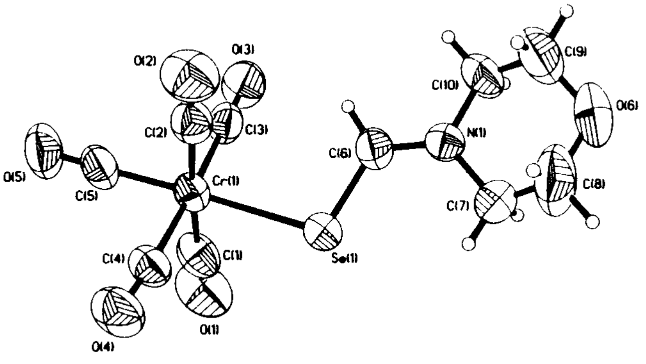


FIGURE 3 ORTEP diagram (50% thermal ellipsoids) of $C_{10}H_9CrNO_6Se$ (2d).

TABLE 4 Selected Bond Lengths (Å) and Angles (deg) for **1a** and **2a**

	Te(1)–C(5)	2.043(9)	N(1)–(1)	1.459(13)
	N(1)–C(5)	1.297(11)	N(1)–C(4)	1.477(11)
1a[a]	N(1)–C(5)–Te(1)	128.6(8)	C(5)–N(1)–C(1)	126.0(8)
	C(5)–N(1)–C(4)	121.6(10)	C(1)–N(1)–C(4)	112.4(8)
	Te(1)–C(6)	2.056(4)	Cr(1)–C(5)	1.843(4)
	N(1)–C(6)	1.297(5)	O(1)–C(1)	1.148(5)
	N(1)–C(7)	1.465(5)	O(2)–C(2)	1.141(5)
2a	N(1)–C(10)	1.485(5)	O(3)–C(3)	1.138(5)
	Cr(1)–C(1)	1.899(4)	O(4)–C(4)	1.140(5)
	Cr(1)–C(2)	1.895(5)	O(5)–C(5)	1.156(5)
	Cr(1)–C(3)	1.891(4)	Te(1)–Cr(1)	2.7076(9)
	Cr(1)–C(4)	1.900(4)		
	N(1)–C(6)–Te(1)	128.0(3)	C(1)–Cr(1)–Te(1)	91.50(12)
	C(6)–N(1)–C(7)	123.8(3)	C(2)–Cr(1)–Te(1)	89.24(12)
	C(6)–N(1)–C(10)	121.9(3)	C(3)–Cr(1)–Te(1)	89.68(12)
	C(7)–N(1)–C(10)	114.2(3)	C(4)–Cr(1)–Te(1)	85.51(13)
	C(6)–Te(1)–Cr(1)	99.67(11)	C(5)–Cr(1)–Te(1)	177.23(14)

[a] Data of **1a** are taken from Ref. [18].

TABLE 5 Selected Bond Lengths (Å) and Angles (deg) for **1b** and **2d**

	Se(1)–C(1)	1.813(7)	N(1)–C(2)	1.478(10)
	N(1)–C(1)	1.302(9)	N(1)–C(5)	1.468(9)
1b	N(1)–C(1)–Se(1)	129.2(6)	C(1)–N(1)–C(5)	122.7(7)
	C(1)–N(1)–C(2)	124.7(6)	C(2)–N(1)–C(5)	112.5(6)
	Se(1)–C(6)	1.815(6)	Cr(1)–C(5)	1.849(7)
	N(1)–C(6)	1.305(7)	O(1)–C(1)	1.154(7)
	N(1)–C(7)	1.446(8)	O(2)–C(2)	1.143(7)
2d	N(1)–C(10)	1.469(7)	O(3)–C(3)	1.138(7)
	Cr(1)–C(1)	1.886(7)	O(4)–C(4)	1.141(6)
	Cr(1)–C(2)	1.898(7)	O(5)–C(5)	1.148(7)
	Cr(1)–C(3)	1.907(7)	Se(1)–Cr(1)	2.5678(11)
	Cr(1)–C(4)	1.907(6)		
	N(1)–C(6)–Se(1)	127.2(4)	C(1)–Cr(1)–Se(1)	86.8(2)
	C(6)–N(1)–C(7)	123.7(5)	C(2)–Cr(1)–Se(1)	89.5(2)
	C(6)–N(1)–C(10)	123.7(5)	C(3)–Cr(1)–Se(1)	92.1(2)
	C(7)–N(1)–C(10)	112.5	C(4)–Cr(1)–Se(1)	90.9(2)
	C(6)–Se(1)–Cr(1)	104.9(2)	C(5)–Cr(1)–Se(1)	178.6(2)

The C–Te bond distance of 2.056 (4) Å in **2a** is only slightly longer than that in **1a** [2.043 (9) Å] and is very close to the average value of 2.06 (3) Å for C–Te double bonds as reported in the CSD database [32]. The Cr-CO_{trans} bond [Cr–C(5), 1.843 (4) Å] is shorter than the Cr–CO_{cis} bonds [1.891 (4)–1.900 (4) Å], while the *trans* C–O bond [C(5)–O(5), 1.156 (5) Å] is longer than all four *cis* C–O bonds [1.138 (5)–1.148 (5) Å]. This is the same as in the cases of a telluroketone tungsten complex [15] and a tellurourea chromium complex [16], in which the *trans* C–O bond is longer than the *cis* C–O bonds. The Cr–Te bond of 2.701 (2) Å is longer than the 2.556 Å covalent bond distance estimated from the Pauling values [32]. This is suggestive of a very weak covalent Cr–Te bond.

The C–Se bond distance [1.813 (7) Å in **1b**] falls well within the range of values reported for C–Se double bonds as found in the CSD database (number reported 162, mean 1.857 (4) Å, range 1.608–2.021 Å) [32]. This distance is virtually unchanged when the selenium is bonded to chromium [1.815 (6) Å in **2d**]. In **2d**, the Cr–CO_{trans} bond [Cr–C(5), 1.849 (7) Å] is shorter than the Cr–CO_{cis} bonds [1.886 (7)–1.907 (7) Å], while the *trans* C–O bond [C(5)–O(5), 1.148 (7) Å] is somewhat longer than three *cis* C–O bonds [1.138 (7)–1.143 (7) Å] but shorter than one *cis* C–O bond [C(1)–O(1), 1.154 (7) Å]. The Cr–Se bond, 2.5678 (11) Å, is much longer than the calculated value of 2.356 Å as estimated from the Pauling tables [33]. Again, this is indicative of a very weak Cr–Se bond.

In the case of nitrogen atoms bonded to tellurocarbonyl or selenocarbonyl carbons, the C–N bond distances are 1.297 (11) Å in **1a**, 1.297 (5) Å in **2a**, 1.302 (9) Å in **1b**, and 1.305 (7) Å in **2d**. All are somewhat longer than the distance of a typical C–N double bond (1.28 Å) [34]. This is indicative of a modest increase in the C–N bond order. The bond angles around the nitrogen atom bonded to telluro- or selenocarbonyl are close to 120°. Based on earlier work [18], form **II** was reasoned to be the most important resonance structure of 4-(telluroformyl)morpholine (**1a**) and 4-(selenoformyl)morpholine (**1b**). However, complexes **2a–2f** are better described by resonance forms **III** and **IV**, and **IV** appears to contribute most to their structures (Scheme 2).

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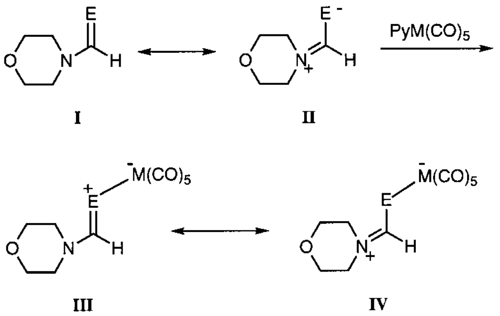
Supporting Information Available

Listings of all bond distances and angles; anisotropic displacement parameters; hydrogen atom coordinates and isotropic displacement parameters for compounds **1b**, **2a**, and **2d** (21 pages); and analytical and spectral data for **1a**, **1b**, and **2a–2f** (41 pages). Ordering information is given on any current masthead page.



SCHEME 2

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