# Preparation of 1,1-Diphenylthionitrosamine and *X*-Ray Crystal Structures of Two Thionitrosamine Complexes †

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The reaction of 1,1-diphenylhydrazine with $S_2Cl_2$ in the presence of triethylamine leads to 1,1-diphenylthionitrosamine. The chromium pentacarbonyl derivative was isolated and characterised by *X*-ray structure determination; $[Cr(SNNPh_2)(CO)_5]$ (2) crystallises in the space group $P2_1/c$ with $a$ = 786.5(1), $b$ = 2 236.5(2), $c$ = 1 054.6(1) pm, β = 89.44(8)°, and $Z$ = 4; $[Cr(SNNMe_2)(CO)_5]$ (3) also crystallises in $P2_1/c$, with $a$ = 1 042.2(3), $b$ = 1 250.7(4), $c$ = 954.6(3) pm, β = 110.21(3)°, and $Z$ = 4. The structures were refined to $R$ = 0.079 for 1 573 diffractometer data with $F > 3\sigma(F)$, and $R$ = 0.049 for 2 388 data with $F > 3\sigma(F)$ respectively. The structures are similar, with $CrSNNC_2$ planes approximately eclipsed to the carbonyls. One of the phenyl groups in (2) can take part in π interaction with the nitrogen atoms, which is associated with longer N–N and shorter S–N and Cr–S bonds in (2) than in (3).

Thionitrosamines [1] are sometimes formed in the reactions of 1,1-disubstituted hydrazines with elemental sulphur. Only 1,1-dimethylthionitrosamine could be prepared in a pure form. We report here the preparation of a new thionitrosamine from disulphur dichloride and 1,1-diphenylhydrazine, and an investigation of thionitrosamine complex formation with transition metals.[2] A preliminary report of the crystal structure of pentacarbonyl(1,1-dimethylthionitrosamine)chromium has already appeared.[2b]

## Experimental

Solvents were refluxed over $P_4O_{10}$ or metallic sodium (tetrahydrofuran or ether respectively) and freshly distilled. 1,1-Dimethyl- and 1,1-diphenyl-hydrazine were analytical grade and used without further purification. All reactions were carried out under dry nitrogen. Infrared spectra were recorded on a Perkin-Elmer 735B spectrophotometer with Nujol mulls, and visible spectra on a Perkin-Elmer 320 spectrophotometer as n-hexane solutions. $^1H$ N.m.r. spectra were recorded using Varian XL-100 and Bruker E-60 spectrometers. 1,1-Dimethylthionitrosamine was prepared as described in the literature.[1]

1,1-*Diphenylthionitrosamine* (1).—$S_2Cl_2$ (1.95 g, 14.5 mmol) was added slowly with stirring to a cooled (−20 °C) solution of $Ph_2NNH_2$ (2.66 g, 14.5 mmol) in diethyl ether (50 $cm^3$) containing $NEt_3$ (3.6 g, 36 mmol). The solution turns deep red with formation of a light yellow precipitate consisting of elemental sulphur and triethylamine hydrochloride. The solid was filtered off, and ether and excess $NEt_3$ were removed from the filtrate under vacuum. The resulting residue was redissolved in light petroleum (30 $cm^3$); the small portion of solid which remained was essentially triethylamine hydrochloride. After removing the light petroleum under vacuum a viscous dark red brown residue remained. The i.r. spectrum showed bands at 3 370w, 1 590vs, 1 500s, 1 410w, 1 305vs, 1 255s, 1 165s, 1 100m, 1 065m, 1 020m, 995w, 935w, 880m, 815w, 745vs, and 685vs $cm^{-1}$. This product was used without further purification.

*Pentacarbonyl*(1,1-*diphenylthionitrosamine*)*chromium* (2).—Compound (1) (1 g) was dissolved in tetrahydrofuran (thf) (40 $cm^3$) and cooled to −20 °C. $[Cr(CO)_5]$·thf (1.14 g, 3.84 mmol) in thf (100 $cm^3$) was added slowly to the stirred solution. After warming to room temperature and stirring for a further 2 h, the solvent was removed *in vacuo*. The deep blue oily residue was dissolved in methylene chloride (50 $cm^3$) and filtered through silicone treated silica gel. The solvent was removed *in vacuo* and the residue recrystallised from n-heptane. Yield, 0.56 g (36%); m.p. 118 °C (decomp.) (Found: C, 49.8; H, 3.0; N, 6.8; S, 7.8. Calc. for $C_{17}H_{10}CrN_2O_5S$: C, 50.25; H, 2.45; N, 6.9; S, 7.9%). I.r.: 2 050m, 1 935s, 1 920s, 1 580w, 1 480m, 1 335m, 1 315m, 1 255s, 1 155w, 1 070w, 1 020m, 1 000w, 965w, 840w, 800w, 765w, 755m, 720m, 690m, and 635s $cm^{-1}$. The $^1H$ n.m.r. spectrum in $CDCl_3$ showed a multiplet at δ 7.08—7.42 p.p.m. relative to $SiMe_4$. U.v. spectrum: 620w, 355w, 270 (sh), and 235s nm. The mass spectrum obtained at 100 °C showed peaks at $m/e$ 406 (relative intensity 2.6%), 350 (1.1), 322 (2.6), 294 (1.7), 266 (25.9), 234 (2.8), 186 (5.4), 168 (100), 154 (7.7), 140 (6.0), 112 (6.0), 84 (20.5), 77 (22.2), 66 (9.4), and 52 (6.8).

*Pentacarbonyl*(1,1-*dimethylthionitrosamine*)*chromium* (3).—A solution of $[Cr(CO)_5]$·thf (2.0 g, 7.5 mmol) in thf (100 $cm^3$) was added to $Me_2NNS$ (0.57 g, 6.3 mmol) [1] at −15 °C. After warming to room temperature and stirring for one further hour, the solvent was removed *in vacuo*. The residue was recrystallised from methylene chloride (25 $cm^3$). $[Cr(CO)_6]$ was removed by sublimation (50 °C, 20 Pa). Yield, 0.4 g of ruby red crystals (24%); m.p. *ca.* 110 °C (decomp.). I.r.: 2 000m, 1 945vs, 1 890vs, 1 360s, 1 260m, 1 120m, 1 090m, 1 020m, 800m, and 785m $cm^{-1}$. The $^1H$ n.m.r. spectrum in $CDCl_3$ showed a singlet at δ 0.41 p.p.m. relative to $SiMe_4$. U.v. spectrum: 535w, 375w, 280 (sh), 250 (sh), and 225s $cm^{-1}$. The mass spectrum obtained at 15 °C showed peaks at $m/e$ 282 (37), 254 (7), 226 (10), 198 (37), 196 (3), 192 (4), 182 (2),

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† *Supplementary data available* (No. SUP 23446, 28 pp.): observed and calculated structure factors, hydrogen atom co-ordinates, isotropic and anisotropic thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

**Table 1.** Crystal data for complexes (2) and (3)

| Formula | $C_{17}H_{10}CrN_2O_5S$ | $C_7H_6CrN_2O_5S$ |
|---|---|---|
| Molecular weight | 406.32 | 282.20 |
| Crystal size (mm) | 0.2 × 0.1 × 0.8 | 0.4 × 0.4 × 0.2 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ |
| Cell dimensions | | |
| $a$/pm | 786.5(1) | 1 042.2(3) |
| $b$/pm | 2 236.5(2) | 1 250.7(4) |
| $c$/pm | 1 054.6(1) | 954.6(3) |
| β/° | 89.44(8) | 110.21(3) |
| $U$/nm$^3$ | 1.8549 | 1.1677 |
| $Z$ | 4 | 4 |
| $D_m$ | not measured | not measured |
| $D_c$/Mg m$^{-3}$ | 1.454 | 1.605 |
| $F$(000) | 824 | 528 |
| μ(Mo-$K_\alpha$)/mm$^{-1}$ | 0.74 | 1.13 |
| Reflections measured | 2 651 | 5 122 |
| Observed Reflections [$F > 3\sigma(F)$] | 1 573 | 2 388 |
| $R$ | 0.079 | 0.049 |
| $R'$ [$= \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}\lvert F_o\rvert$] | 0.068 | 0.044 |
| Weighting scheme ($w^{-1}$) | $\sigma^2(F) + 0.0005\lvert F_o\rvert^2$ | $\sigma^2(F) + 0.0002\lvert F_o\rvert^2$ |
| Maximum residual electron density (pm$^{-3}$) | 3.8 × 10$^{-7}$ | 3.4 × 10$^{-7}$ |

**Table 2.** Atomic co-ordinates (× 10$^4$) for (2) with estimated standard deviations in parentheses

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Cr | 2 649(2) | 531(1) | 2 607(1) |
| S | 2 813(3) | 1 580(1) | 2 446(2) |
| N(2) | 4 394(7) | 1 723(2) | 1 511(5) |
| N(1) | 4 766(7) | 2 280(2) | 1 202(5) |
| C(11) | 4 803(12) | 421(3) | 1 825(10) |
| C(12) | 566(12) | 575(3) | 3 432(10) |
| O(11) | 6 065(9) | 356(3) | 1 325(10) |
| O(12) | −724(9) | 567(3) | 3 928(9) |
| C(13) | 1 544(12) | 540(4) | 992(8) |
| C(14) | 2 479(10) | −291(3) | 2 729(8) |
| C(15) | 3 794(13) | 597(3) | 4 221(9) |
| O(13) | 860(12) | 563(4) | 55(8) |
| O(14) | 2 376(7) | −803(3) | 2 811(7) |
| O(15) | 4 475(10) | 626(3) | 5 176(7) |
| C(2) | 4 359(10) | 3 148(3) | 2 534(7) |
| C(3) | 3 428(11) | 3 637(4) | 2 909(8) |
| C(4) | 1 896(11) | 3 749(4) | 2 367(9) |
| C(5) | 1 287(10) | 3 383(4) | 1 413(9) |
| C(6) | 2 227(8) | 2 890(3) | 1 011(7) |
| C(1) | 3 762(8) | 2 780(3) | 1 606(7) |
| C(2′) | 7 342(9) | 1 902(3) | 225(7) |
| C(3′) | 8 640(9) | 1 984(4) | −622(8) |
| C(4′) | 8 836(10) | 2 512(4) | −1 251(8) |
| C(5′) | 7 691(10) | 2 967(4) | −1 059(8) |
| C(6′) | 6 385(10) | 2 900(4) | −219(7) |
| C(1′) | 6 196(8) | 2 366(3) | 423(7) |

**Table 3.** Atomic co-ordinates (× 10$^5$) for (3) with estimated standard deviations in parentheses

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Cr | 25 007(3) | 37 711(3) | 44 301(4) |
| S | 7 247(6) | 37 410(5) | 20 476(6) |
| N(1) | −7 563(18) | 37 196(13) | 22 834(20) |
| N(2) | −18 409(19) | 37 013(14) | 11 272(21) |
| C(11) | −31 419(26) | 37 271(23) | 13 849(33) |
| C(12) | −18 348(29) | 36 817(24) | −3 857(28) |
| C(1) | 24 580(25) | 22 438(21) | 44 682(26) |
| O(1) | 24 819(22) | 13 416(14) | 44 843(22) |
| C(2) | 12 083(26) | 38 636(17) | 54 399(27) |
| O(2) | 4 631(20) | 39 364(14) | 60 659(21) |
| C(3) | 37 907(25) | 37 026(18) | 34 473(29) |
| O(3) | 46 126(20) | 36 732(15) | 29 070(25) |
| C(4) | 25 389(23) | 52 873(21) | 43 206(25) |
| O(4) | 25 938(20) | 61 886(13) | 42 649(23) |
| C(5) | 39 156(26) | 37 925(19) | 62 423(29) |
| O(5) | 47 866(20) | 38 208(14) | 73 824(22) |

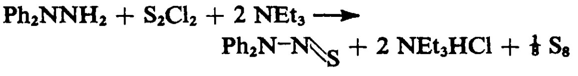
170 (3), 168 (7), 154 (4), 142 (100), 140 (14), 127 (4), 126 (8), 112 (46), 108 (9), 98 (28), 90 (16), 84 (7), 80 (25), 75 (6), 58 (7), 52 (72), 46 (3), 44 (16), and 43 (49).

*X-Ray Structural Analysis.*—Intensities were measured for both compounds on a Stoe four-circle diffractometer for $7 < 2\theta < 50°$ using graphite monochromated Mo-$K_\alpha$ radiation ($\lambda = 71.069$ pm) and a profile fitting procedure.[3] Crystal data for (2) and (3) are summarised in Table 1. Lorentz-polarisation and semi-empirical absorption corrections were applied to both data sets. The structures were solved by direct [compound (2)] and Patterson [compound (3)] methods. A riding model was applied for hydrogen atom refinement (C–H 96 pm) with rigid methyl groups (C–H 96 pm, H–C–H 109.5°) and fixed [compound (2)] and refined [compound (3)] isotropic hydrogen atom temperature factors. The structures were refined with the remaining atoms anisotropic by blocked-cascade least squares using complex neutral-atom scattering factors. A Data General Eclipse mini-computer was employed for all calculations, using programs written by G. M. Sheldrick.

Final atomic co-ordinates are given in Tables 2 and 3, and selected molecular dimensions are compared in Table 4.

## Results and Discussion

The reaction of 1,1-dimethylhydrazine and elemental sulphur results in the formation of 1,1-dimethylthionitrosamine. Under the reaction conditions reported, this was the only thionitrosamine which could be prepared analytically pure. This compound is stable only at low temperatures or in dilute solution in a non-polar solvent; neat liquid samples decompose at room temperature within a few hours. In contrast, 1,1-diphenylhydrazine does not react with elemental sulphur in diethyl ether. The rapid decomposition of thionitrosamines by acidic materials prevents the direct reaction of hydrazines with disulphur dichloride with elimination of hydrogen chloride. In the case of 1,1-diphenylhydrazine triethylamine was used to trap the hydrogen chloride, equation (i).



$$Ph_2NNH_2 + S_2Cl_2 + 2\,NEt_3 \longrightarrow Ph_2N{-}N{=}S + 2\,NEt_3HCl + \tfrac{1}{8}\,S_8 \quad \text{(i)}$$

Compound (1) is not stable enough for purification by recrystallisation or sublimation, but could be isolated as the

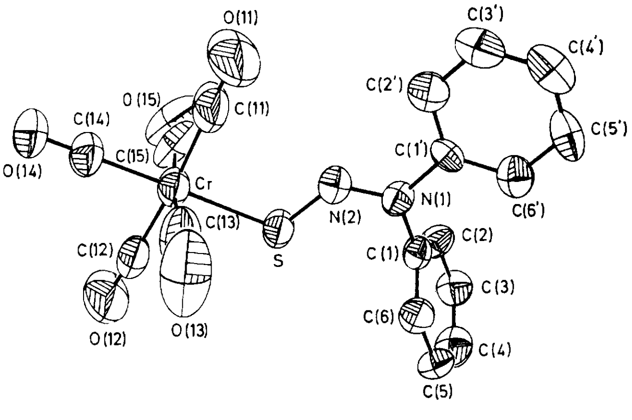


**Figure 1.** Molecular structure of [Cr(SNNPh$_2$)(CO)$_5$] (2) showing the atom numbering scheme and 50% probability thermal ellipsoids

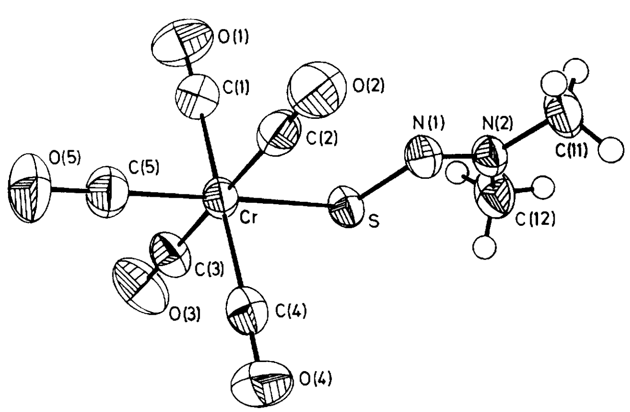


**Figure 2.** Molecular structure of [Cr(SNNMe$_2$)(CO)$_5$] (3) showing the atom numbering scheme and 50% probability thermal ellipsoids

chromium pentacarbonyl complex (2) by treating it with [Cr(CO)$_5$]·thf. Compound (2) is deep blue in colour and stable against moisture and air at room temperature. On the basis of vibrational spectroscopy it was not clear which atom of the ligand co-ordinates to the chromium. For comparison the 1,1-dimethylthionitrosamine complex (3) was prepared. Compound (3) is ruby red and of comparable stability. Both are soluble in all common organic solvents, except carbon tetrachloride, without noticeable decomposition. In carbon tetrachloride the formation of the free ligand Me$_2$NNS was observed. The 1,1-diphenylthionitrosamine complex is sensitive to light and decomposes on prolonged exposure to daylight.

In the i.r. spectrum ν(NS) is shifted from 915 cm$^{-1}$ in the free ligand to 785 cm$^{-1}$ in (3), indicating that complex formation through S weakens the N–S bond.

The mass spectra of both complexes show molecular ions at *m*/*e* 406 and 282, respectively. The carbonyl groups are lost successively. The CrSNNR$_2$ fragments have the highest relative intensity. The peaks at *m*/*e* 84 (CrS) suggested that the ligands are bonded to chromium *via* sulphur. An unambiguous assignment could only be made by the *X*-ray structural investigation.

**Table 4.** Selected bond lengths (pm), angles (°), and torsion angles (°) in compounds (2) and (3)

| | (2) | (3) |
|---|---|---|
| Cr–C (*trans*) | 184.8(7) | 184.6(2) |
| Cr–C (*cis*, mean) | 190.0(9) | 190.3(5) |
| C–O (mean) | 113.9(12) | 113.8(4) |
| Cr–S | 235.7(2) | 238.6(1) |
| S–N | 161.2(6) | 163.5(2) |
| N–N | 131.9(7) | 127.9(2) |
| N–C (*cis*) | 143.2(8) | 144.6(4) |
| N–C (*trans*) | 140.0(9) | 146.0(4) |
| S–Cr–C (*cis*, mean) | 89.9(10) | 89.8(2) |
| Cr–S–N | 106.4(2) | 109.1(1) |
| S–N–N | 120.4(4) | 118.5(2) |
| N–N–C (*cis*) | 116.7(5) | 123.7(2) |
| N–N–C (*trans*) | 120.3(5) | 116.7(2) |
| C(eclipsed)–Cr–S–N | 12.1(4) | −4.1(1) |
| Cr–S–N–N | 177.6(5) | 180.0(1) |
| S–N–N–C (*cis*) | 177.7(4) | −177.6(2) |
| S–N–N–C (*trans*) | −3.6(9) | 1.0(3) |

The two molecular structures are similar, the more precise results for (3) being due to the better crystal quality. In both cases the CrSNNC$_2$ units are effectively planar, and these planes lie approximately eclipsed to the carbonyl groups, as may be seen in the torsion angles quoted in Table 4. The mean S–Cr–C (*cis*) angles are very close to 90°, indicating π back-bonding with the ligand to the same extent as with the carbonyls. However, there is also a marked *trans* effect on the Cr–C bond lengths. The *trans* phenyl group in (2) lies approximately in the CrSNNC$_2$ plane, and the *trans* N–C bond is 3.2 pm shorter than the *cis*, indicating π interaction between the *trans* phenyl ring and the nitrogen atoms. This is associated with a significant lengthening of the N–N bond, and shortening of the N–S and Cr–S bonds, in (2) compared with (3). Despite the different substituents, the packing of the molecules in the crystal is similar in the two structures, with no short intermolecular interactions.

## Acknowledgements

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